

# Theoretical investigations on Ziegler–Natta catalysis: Coordination of the electron donors to titanium modified $\text{MgCl}_2$ support

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## Abstract

Theoretical *ab initio* methods have been used to study the formation of the support-catalyst complex and the coordination of electron donors to this complex. A  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster was used to model the catalyst surface. Determination of the coordination geometry of the supported catalyst indicated that the  $\text{TiCl}_4$  catalyst coordinates octahedrally to the surface of the support, leaving one coordination site of the titanium empty. This vacant coordination site is in a stereospecific position. The coordination of different electron donors (alcohols, ketones, esters and their model compounds) through their oxygen atom to the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster was also studied. On the basis of the interaction energies, released in the coordination of the donors, the alcohol donors bind more strongly to the support than the ketones and esters. The extra stability of the alcohols can be explained by hydrogen bonding. The coordination geometries of the electron donors studied can be estimated rather reliably even with small model compounds.

*Keywords:* Ziegler–Natta; *Ab initio*; Magnesium chloride support; Titanium catalyst; Electron donor; Alcohol; Ketone; Ester

## 1. Introduction

The Ziegler–Natta catalysts, based on the  $\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$  catalyst system, are generally used in the polymerization of  $\alpha$ -olefins. In particular, the industrial production of isotactic polypropylene with high activity and stereospecificity is dependent on these catalysts [1,2]. The development of the commercial Ziegler–

Natta catalyst systems has been mainly based on experimental work, but improvement of computational methods has also made theoretical investigations of these systems at the molecular level possible.

In theoretical studies for Ziegler–Natta type systems the most often investigated subjects have been the nature of the titanium–alkyl bond [3–10] and the growth mechanism of the polymer chain in the coordination sphere of the titanium atom [11–21]. On the basis of these studies, there is a fairly good conception of the insertion mechanism of olefins into the transi-

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tion metal alkyl bond of the catalyst during the polymerization reaction. In addition to the catalyst, the progress of the heterogeneous polymerization reaction also depends on the support material of the catalyst and the existence of various electron donors, which have not been taken into account in the theoretical studies.

In the present paper we describe an ab initio study in which the formation of the support–catalyst complex and the coordination of the electron donors to this complex have been studied. Previously, the interaction between the support and the catalyst has been investigated using density functional theory [22] and Hartree–Fock [23] calculations. In the former study the coordination of the  $\text{TiCl}_4$  catalyst to the five-coordinated (101) surface of the  $\text{MgCl}_2$  support was examined. In the latter study we studied the interaction between the  $\text{TiCl}_4$  catalyst and the  $\text{MgCl}_2$  support without restricting the investigations to the specific surfaces of  $\text{MgCl}_2$ . We demonstrated that the tetrahedral  $\text{TiCl}_4$  can coordinate to the four-coordinated (110) surface of  $\text{MgCl}_2$ . Based on these results, we have continued our study by investigating the coordination of the  $\text{TiCl}_4$  catalyst to the surface of the support model (a  $\text{Mg}_4\text{Cl}_8$  cluster) cut from the (110) surface of  $\text{MgCl}_2$ .

Earlier we also studied theoretically the coordination of the organic electron donors to the surface of the  $\text{MgCl}_2$  support [24]. Understanding the properties of the electron donors is important because the capability of the electron donors to affect the activity and stereospecificity of the catalyst depends on their structural and electronic properties. The coordination of the electron donors (alcohols, ketones, esters and their model compounds) through oxygen to the magnesium atom on the (110) and (101) surfaces of  $\text{MgCl}_2$  was investigated in order to understand the dependence of the coordination of the electron donors on the surface of  $\text{MgCl}_2$  and on the number of the electron donors on the same magnesium atom. In the present study we have continued to examine the coordination of different electron donors, now to the surface of

the  $\text{Mg}_4\text{Cl}_8$  support model in the absence and presence of the  $\text{TiCl}_4$  catalyst.

## 2. Computational methods

The ab initio calculations reported here were carried out with the Gaussian 92 computer program [25] at the restricted Hartree–Fock level of theory with the 3-21G basis set. Because the standard basis sets of the program do not include split-valence basis sets for transition metals, the Dobbs and Hehre's 3-21G basis set [26] was used for the titanium atom. The influence of the basis sets on the results has not been tested in this study, but according to earlier results [24,26,27] we have assumed that the 3-21G basis set generally predicts geometrical parameters in good accord with experimental values, although Ti–Cl and C–O bond lengths are overestimated (about 2–4 pm) and Mg–O bond lengths are underestimated (about 7 pm). Further, energy values, calculated with the 3-21G basis set, are of the same order as the corresponding energy values using the 6-31G basis set, when the BSSE correction is taken into account.

The coordination geometry between the support and the catalyst was determined by partially optimizing the geometry of the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  support–catalyst complex. While the geometrical parameters of the catalyst ( $\text{TiCl}_4$ ) were optimized, the geometrical parameters of the support model ( $\text{Mg}_4\text{Cl}_8$ ) were fixed to those in the bulk crystal structure [28] of  $\text{MgCl}_2$ . After the structure of the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster was defined, the coordination geometry of the electron donors was determined using the same method as for the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster. The geometrical parameters of the electron donors were fully optimized, but the geometry of the  $\text{Mg}_4\text{Cl}_8$  or  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster was kept fixed.

The stability of the different complexes was estimated by examining interaction energies, which are released in the coordination of the

electron donors to the  $\text{Mg}_4\text{Cl}_8$  or  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster. The interaction energy  $\Delta E$  is calculated using the following equation:

$$\Delta E = E_{\text{tot}} - \sum_i E_i \quad (1)$$

where  $E_{\text{tot}}$  = the total energy of the complex and  $\sum_i E_i$  = the sum of the total energies of the components [29,30].

The interaction energies are dependent on the order of the basis set superposition error (BSSE), which can be calculated with the counterpoise method [29,30]. The effect of the BSSE on the interaction energies was taken into account with the equation:

$$\Delta E^{\text{BSSE}} = \Delta E + \text{BSSE} \quad (2)$$

in which  $\Delta E^{\text{BSSE}}$  = the interaction energy corrected for the BSSE.

### 3. Results and discussion

#### 3.1. Formation of the support–catalyst complex

In the first part of the study we investigated the coordination of the  $\text{TiCl}_4$  catalyst to the surface of the  $\text{MgCl}_2$  support. The catalyst coordinates to such surfaces of  $\text{MgCl}_2$  in which the coordination sphere of the magnesium atoms is not fully occupied [22,31]. Such surfaces are, e.g., the (100), (101), (104) and (110) planes of  $\text{MgCl}_2$ . On the (100) surface the magnesium atoms are either three-, five- or six-coordinated. However, after the surface reconstruction the magnesium atoms on this surface are most likely five-coordinated [22]. On the (101) and (104) surfaces the magnesium atoms are also five-coordinated. The (104) surface is atomically flat like that of the (110) surface, where the magnesium atoms are four-coordinated.

Based on these statements, typical examples of surfaces with vacant coordination sites are the (101) surface with five-coordinated magnesium atoms and the (110) surface with four-coordinated magnesium atoms. Because our ear-

lier study [23] showed that the tetrahedral  $\text{TiCl}_4$  catalyst can coordinate to the four-coordinated magnesium atom, we continued this study by examining the coordination of the catalyst to the surface of the  $\text{Mg}_4\text{Cl}_8$  cluster cut from the (110) surface of  $\text{MgCl}_2$ . The effect of the surrounding ionic crystal was not taken into account, because the coordination of the catalyst to the support surface is supposed to be a local phenomenon. A point charge model for the surrounding ionic crystal could be considered, but the arbitrariness of the placement of the respective surface charges would have made the model very ambiguous. The present model should be considered only qualitative anyway.

A determination of the coordination geometry of the catalyst and the support model indicates that the  $\text{TiCl}_4$  catalyst coordinates to the four-coordinated magnesium atom with three chlorine bridges (Fig. 1). When the coordination sphere of the magnesium atom is completed with the chlorine atoms of the  $\text{TiCl}_4$  catalyst, the geometric structure of the  $\text{TiCl}_4$  changes from tetrahedral to octahedral. A corresponding result was also obtained in our earlier investigation [23].

A comparison of the geometrical parameters in the coordination sphere of the titanium atom

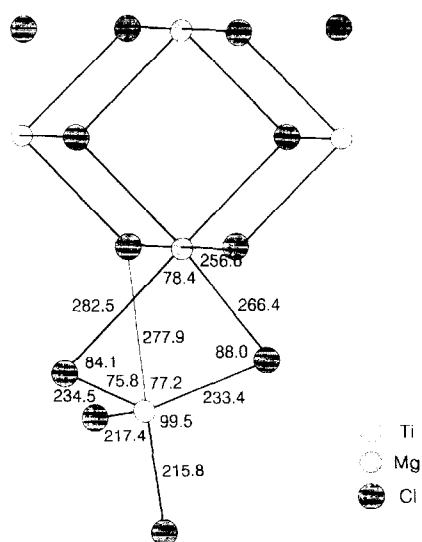


Fig. 1. The  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster.

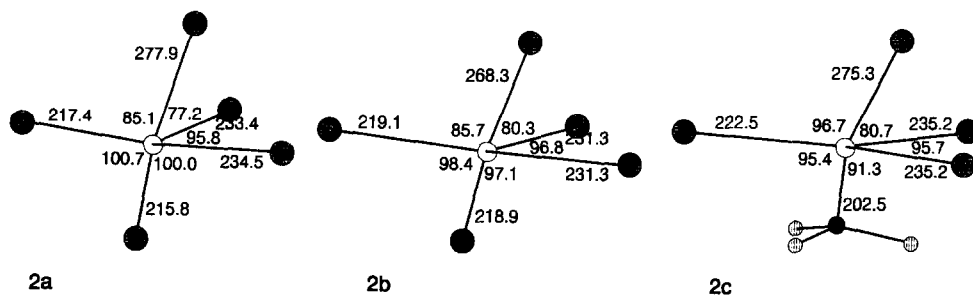


Fig. 2. The coordination sphere of the titanium atom in  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  (a),  $\text{MgCl}_2\text{TiCl}_4$  (b) and  $\text{MgCl}_2\text{TiCl}_3\text{CH}_3$  (c).

(Fig. 2) indicates that our present and earlier [23] investigations support each other. The terminal Ti–Cl bond lengths are generally 216–219 pm, only in the case of  $\text{MgCl}_2\text{TiCl}_3\text{CH}_3$  is it slightly longer, 223 pm. The bridging Ti–Cl bond lengths can be divided into two groups: the lengths of two bonds are 231–235 pm and the length of the third is 268–278 pm. The Cl–Ti–Cl bond angles vary from  $77^\circ$  to  $101^\circ$ , but the maximum deviation in the individual bond angle is only  $12^\circ$ . On the basis of these results the coordination geometry determined for the  $\text{TiCl}_4$  catalyst on the  $\text{MgCl}_2$  support does not depend on the size of the support model ( $\text{Mg}_4\text{Cl}_8$  or  $\text{MgCl}_2$ ). It is typical of this coordination geometry that the titanium atom has octahedral bonding geometry with one vacant site. Because this vacant site is stereochemically in a specific position, the support–catalyst complex can act as a stereospecific catalyst in olefin polymerization.

### 3.2. Coordination of the electron donors

In the second part of the study we investigated the coordination of different electron donors to the surface of the  $\text{MgCl}_2$  support in the absence and presence of the  $\text{TiCl}_4$  catalyst. We used the same support model, the  $\text{Mg}_4\text{Cl}_8$  cluster, as before. Because this model contains two four-coordinated magnesium atoms, it is the smallest possible support model that can be used in considering the effect of the electron donors in the presence of the titanium catalyst at a qualitative level. Since there is no experimen-

tal evidence of the direct interaction between the electron donors and the titanium center, it is from the theoretical viewpoint more feasible to examine the coordination of the electron donors with the support model, where the magnesium atoms are on opposite sides of the model, than to enlarge the support model so that the electron donors can be placed beside adjacent to the catalyst. On account of this, the consideration of the steric effects of the catalyst to the coordination of the electron donors is avoided. Further, the coordination of the electron donors to the support surface is supposed to be a local phenomenon, and therefore the effect of the surrounding ionic crystal was not taken into account in this study.

We examined the coordination of two electron donors (two alcohol, ketone, ester or their model molecules) to the same four-coordinated magnesium atom in order to fill the coordination sphere of the magnesium atom. The four-coordinated magnesium atom on the opposite side of the  $\text{Mg}_4\text{Cl}_8$  cluster was occupied by the titanium catalyst. In the case of the alcohols, we studied the coordination of water ( $\text{H}_2\text{O}$ ), methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) molecules to this  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  support–catalyst complex. Of these compounds the water molecule is the smallest model compound that can be used to estimate the coordination mode of alcohols with the support material; the ethanol molecule is the smallest alcohol used as the real electron donor in the catalysis.

The examination of ketones was performed by studying the properties of formaldehyde

Table 1

Interaction energies corrected for the BSSE ( $\Delta E(\text{BSSE})$ ) and geometrical parameters for the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster with water, methanol and ethanol using the 3-21G basis set

	$\Delta E(\text{BSSE})$ (kJ/mol)	Donor	$r(\text{Mg}-\text{O})$ (pm) complexed	$r(\text{X}-\text{O})^a$ (pm)		$r(\text{O}-\text{H})$ (pm)		$\angle(\text{X}-\text{O}-\text{H})^a$ ( $^\circ$ )		Coordination angle ( $^\circ$ ) <sup>b</sup> complexed
				free	complexed	free	complexed	free	complexed	
$\text{Mg}_4\text{Cl}_8\text{TiCl}_4-(\text{H}_2\text{O})_2$	-466.1	1st	199.64	96.39	97.39	96.63	103.59	107.8	109.0	32.2
		2nd	199.38		97.36		103.28		109.5	32.7
$\text{Mg}_4\text{Cl}_8\text{TiCl}_4-(\text{CH}_3\text{OH})_2$	-456.5	1st	199.10	144.09	145.81	96.58	102.72	110.3	109.1	31.9
		2nd	198.80		145.71		102.45		109.7	32.5
$\text{Mg}_4\text{Cl}_8\text{TiCl}_4-(\text{CH}_3\text{CH}_2\text{OH})_2$	-431.8	1st	198.42	144.43	146.81	96.61	102.20	110.9	109.1	32.7
		2nd	199.18		145.80		102.09		109.5	32.9
		Exptl. <sup>c</sup>	207.0		143.3		70.0		104.9	

<sup>a</sup> X = C, except in  $\text{H}_2\text{O}$  X = H.

<sup>b</sup> Angle, defined in Ref. [24], between the donor and the support surface.

<sup>c</sup>  $\text{MgCl}_2-(\text{CH}_3\text{CH}_2\text{OH})_6$  crystal in Ref. [32].

(HCOH), acetaldehyde ( $\text{CH}_3\text{COH}$ ) and acetone ( $\text{CH}_3\text{COCH}_3$ ) molecules. Of these compounds the acetone is the smallest ketone, used as the electron donor in the catalysis, while the formaldehyde and acetaldehyde molecules were used as the model compounds for ketones. Correspondingly, the examination of esters was performed by studying the properties of the smallest ester compounds, methylformate ( $\text{HCOOCH}_3$ ) and ethylformate ( $\text{HCOOCH}_2\text{CH}_3$ ) molecules, and their model compound, formic acid (HCOOH).

The interaction energies released in the coordination of these electron donors with the support-catalyst complex and the geometrical parameters of the free and complexed electron

donors are shown in Table 1 for alcohols, in Table 2 for ketones and in Table 3 for esters.

A comparison of the interaction energies indicates that the alcohols form more stable complexes with the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster than the ketones and esters. The stability of the alcohols can be explained by the hydrogen bonding between the complexed alcohol and a chloride ion (Fig. 3). The  $\text{O}-\text{H}\cdots\text{Cl}^-$  hydrogen bond length varies from 212.0 pm to 217.0 pm; it is shortest for the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4-(\text{H}_2\text{O})_2$  complex, where the O-H bond length is also longer than in the other alcohol complexes.

A comparison of the geometrical parameters of the free and complexed electron donors indicates that the following details are typical of

Table 2

Interaction energies corrected for the BSSE ( $\Delta E(\text{BSSE})$ ) and geometrical parameters for the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster with formaldehyde, acetaldehyde and acetone using the 3-21G basis set

	$\Delta E(\text{BSSE})$ (kJ/mol)	Donor	$r(\text{Mg}-\text{O})$ (pm) complexed	$r(\text{C}-\text{O})$ (pm)		$r(\text{C}-\text{X})^a$ (pm)		$\angle(\text{X}-\text{C}-\text{Y})^{a,b}$ ( $^\circ$ )		Coordination angle ( $^\circ$ ) complexed
				free	complexed	free	complexed	free	complexed	
$\text{Mg}_4\text{Cl}_8\text{TiCl}_4-(\text{HCOH})_2$	-438.8	1st	195.26	120.69	126.20	108.32	107.37	114.9	117.6	34.1
		2nd	195.16		125.85		107.40		117.6	34.9
$\text{Mg}_4\text{Cl}_8\text{TiCl}_4-(\text{CH}_3\text{COH})_2$	-379.8	1st	194.33	120.84	125.52	150.69	149.89	114.3	117.7	34.6
		2nd	194.10		125.22		149.87		117.7	35.6
$\text{Mg}_4\text{Cl}_8\text{TiCl}_4-(\text{CH}_3\text{COCH}_3)_2$	-357.5	1st	195.51	121.10	124.14	151.50	149.69	115.1	117.6	38.8
		2nd	195.27		124.03		149.75		117.6	39.7

<sup>a</sup> X = C, except in HCOH X = H.

<sup>b</sup> Y = H, except in  $\text{CH}_3\text{COCH}_3$  Y = C.

Table 3

Interaction energies corrected for the BSSE ( $\Delta E(\text{BSSE})$ ) and geometrical parameters for the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster with formic acid, methylformate and ethylformate using the 3-21G basis set

	$\Delta E(\text{BSSE})$ (kJ/mol)	Donor	$r(\text{Mg}-\text{O}_1)$ (pm) complexed	$r(\text{C}-\text{O}_1)$ (pm)		$r(\text{C}-\text{O}_2)$ (pm)		$\angle(\text{H}-\text{C}-\text{O}_2)$ ( $^\circ$ )		Coordination angle ( $^\circ$ ) complexed
				free	complexed	free	complexed	free	complexed	
$\text{Mg}_4\text{Cl}_8\text{TiCl}_4-(\text{HCOOH})_2$	-371.9	1st	196.33	119.77	124.65	135.02	131.77	109.5	113.9	38.5
		2nd	196.18		124.42		131.73		113.8	39.4
$\text{Mg}_4\text{Cl}_8\text{TiCl}_4-(\text{HCOOCH}_3)_2$	-364.4	1st	195.77	120.00	124.67	134.35	130.80	109.9	113.6	37.4
		2nd	195.62		124.48		130.72		113.5	38.1
$\text{Mg}_4\text{Cl}_8\text{TiCl}_4-(\text{HCOOCH}_2\text{CH}_3)_2$	-353.2	1st	195.49	120.06	124.66	134.23	130.59	110.1	113.6	38.3
		2nd	195.31		124.48		130.54		113.5	39.0

these donors. The coordination distance between the electron donor and the surface does not depend much on the type of donor, because the maximum deviation in the  $\text{Mg}-\text{O}$  bond length between different complexes is only 6 pm. The  $\text{C}-\text{O}$  and  $\text{O}-\text{H}$  bond lengths in the alcohols and the  $\text{C}-\text{O}$  bond length of the carbonyl group in the aldehydes and ketones are longer in the complexed donor than in the free donor. The oxygen of the alkoxy group in the esters is more strongly bound to the carbon of the carbonyl group in the complexed donor than in the free donor. The coordination angle between the donor and the surface is generally  $32-40^\circ$  in these complexes. Based on these results, the estimation of the structural changes

taking place during the coordination of these alcohol, ketone and ester donors can usually be made rather reliably, even with small model compounds, as the earlier study [24] also indicated.

Finally, we estimated the dependence of the above results on the size of the support model and the presence of the titanium catalyst. We examined the coordination of two water, formaldehyde and acetone molecules to the four-coordinated magnesium atom of the  $\text{Mg}_4\text{Cl}_8$  cluster in the absence of the catalyst. The geometrical parameters and the interaction energies for these donors complexed with the  $\text{Mg}_5\text{Cl}_{10}$  [24],  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  and  $\text{Mg}_4\text{Cl}_8$  clusters are shown in Table 4.

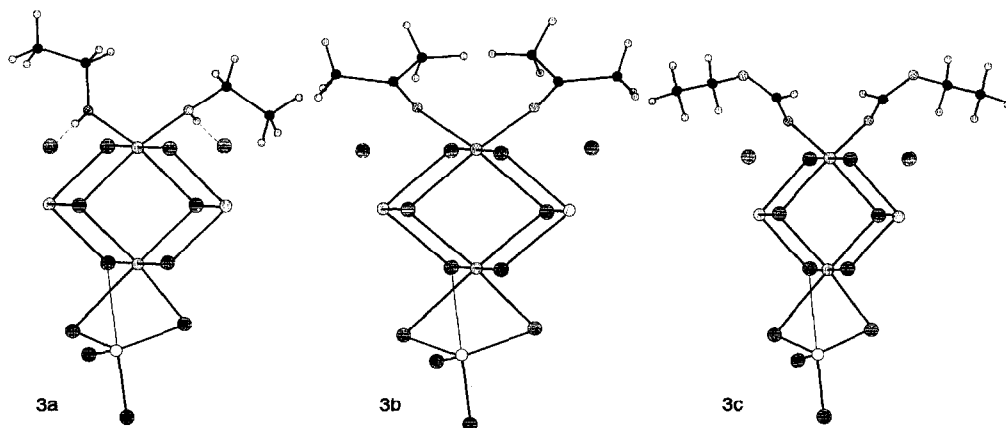


Fig. 3. Coordination of ethanol (a), acetone (b) and ethylformate (c) molecules to the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster.

A comparison of these geometrical results reveals some typical features of these complexes. The Mg–O bond lengths of the water molecules are not dependent on the support model. The water forms the hydrogen bonds with the unconnected chloride ions of the  $\text{Mg}_4\text{Cl}_8$  and  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  clusters. As a result of the hydrogen bonding, one O–H bond of the water is about 6 pm longer than the other. For the  $\text{Mg}_4\text{Cl}_8$  and  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  clusters the coordination angle formed between the donor and the support surface is due to the hydrogen bonding being smaller than that of the  $\text{Mg}_5\text{Cl}_{10}$  cluster. For the  $\text{Mg}_5\text{Cl}_{10}$  cluster the electron donors coordinate to four-coordinated magnesium atoms on the layer where hydrogen bond formation is not possible. On the other hand, the structures of the acetone and formaldehyde complexes are nearly independent of the support models.

The estimation of the stability of the electron

donors can be made fairly well by using all of these support models. The presence of the titanium catalyst on the support cluster only slightly affects the stability of these donor complexes; it weakens (about 2–11%) the interaction between the donors and the support when compared to the bare support. Our results show that the effect of the support model is more significant than that of the catalyst. Since the effect of the titanium catalyst on the interaction energies of the donor complexes is minor, the comparison of the energies of the donors has been made between the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  and  $\text{Mg}_5\text{Cl}_{10}$  clusters. The ketone and ester donors are 6–18% more stable on the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster than on the  $\text{Mg}_5\text{Cl}_{10}$  cluster, but the alcohols bind almost 40% more strongly to the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster than to the  $\text{Mg}_5\text{Cl}_{10}$  cluster. This extraordinary stability of the alcohols with the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster can be explained by the hydrogen bonding: on the  $\text{Mg}_5\text{Cl}_{10}$  cluster the

Table 4

Interaction energies corrected for BSSE ( $\Delta E(\text{BSSE})$ ) and geometrical parameters using the 3-21G basis set for water, formaldehyde and acetone complexed with the  $\text{Mg}_5\text{Cl}_{10}$ ,  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  and  $\text{Mg}_4\text{Cl}_8$  clusters

	Support model	$\Delta E(\text{BSSE})$ (kJ/mol)	Donor	$r(\text{Mg}-\text{O})$ (pm)	$r(\text{O}-\text{X})^a$ (pm)	Hydrogen bond (pm)	Coordination angle ( $^\circ$ )
$\text{H}_2\text{O}$	$\text{Mg}_5\text{Cl}_{10}$	–335.5	1st	199.6	97.0		41.7
			2nd	199.9	96.5		40.6
	$\text{Mg}_4\text{Cl}_8\text{TiCl}_4$	–466.1	1st	199.6	97.2		32.2
			2nd	199.4	97.4	211.5	32.7
	$\text{Mg}_4\text{Cl}_8$	–500.6	1st	199.3	103.6	212.6	32.6
			2nd	199.3	97.4	213.6	32.5
$\text{HCOH}$	$\text{Mg}_5\text{Cl}_{10}$	–305.7	1st	201.8	102.0	213.6	38.7
			2nd	201.9	96.4		38.3
	$\text{Mg}_4\text{Cl}_8\text{TiCl}_4$	–438.8	1st	195.3	122.8		34.1
			2nd	195.2	123.0		34.9
	$\text{Mg}_4\text{Cl}_8$	–449.2	1st	195.2	126.2		34.1
			2nd	195.2	125.8		34.1
$\text{CH}_3\text{COCH}_3$	$\text{Mg}_5\text{Cl}_{10}$	–338.7	1st	198.1	126.2		39.1
			2nd	198.4	123.8		38.4
	$\text{Mg}_4\text{Cl}_8\text{TiCl}_4$	–357.5	1st	195.5	124.0		38.8
			2nd	195.3	124.1		39.7
	$\text{Mg}_4\text{Cl}_8$	–400.2	1st	195.3	124.1		39.1
			2nd	195.3	124.1		39.1

<sup>a</sup> X = C, except in  $\text{H}_2\text{O}$  X = H.

alcohols cannot form hydrogen bonds, but on the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  cluster they form hydrogen bonds with the unconnected chloride ions on the layer of the surface ions. On account of this, the hydrogen bonding emphasizes the effect of the support model on the stability of the alcohol complexes. On the real support surface the coordination of the alcohol donors to the four-coordinated magnesium atom is a compromise between their coordination to the surface of the  $\text{Mg}_5\text{Cl}_{10}$  and  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  clusters. Anyway, the alcohols generally form more stable complexes on the support surfaces than the ketones or esters, and the stability of the alcohols depends on the possibility of forming hydrogen bonds.

#### 4. Conclusions

The formation of the  $\text{Mg}_4\text{Cl}_8\text{TiCl}_4$  support-catalyst complex indicates that the  $\text{TiCl}_4$  catalyst changes its geometry from tetrahedral to octahedral in the coordination to the surface of the  $\text{MgCl}_2$  support. This structure is relatively stable, although the titanium has one vacant coordination site. The stability of different electron donors with this support-catalyst complex depends on the existence of hydrogen bonds. These bonds are typical of alcohols, but not ketones and esters.

#### Acknowledgements

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