Theoretical Investigations on Heterogeneous Ziegler−Natta Catalyst Supports: Stability of the Electron Donors at Different Coordination Sites of $MgCl_2$

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Ab initio methods were used to study the coordination of electron donors to the (110) and (101) surfaces of a $MgCl_2$ support. The electron donors were alcohols, ketones, esters, and their model compounds. Examination of the interaction energies indicated that the alcohols bind more strongly to the five-coordinated magnesium atom on the (101) surface than to the four-coordinated magnesium atom on the (110) surface. This stability on the (101) surface can be explained in terms of hydrogen bonding between the complexed alcohol and a chloride ion of the surface. Like the alcohols, the esters form the most stable complexes on the (101) surface. In contrast, the ketones coordinate preferably to the (110) surface. The geometries of these coordinated electron donors can be predicted fairly reliably even with small model compounds. In the case of the alcohols, the coordination angle between the donor and the surface depends on the number of alcohols on the same magnesium atom.

1. Introduction

In the modern Ziegler−Natta catalyst system the $TiCl_4$ catalyst is supported on the $MgCl_2$ surface in the presence of internal electron donors, and the aluminum alkyl cocatalyst is complexed with an external electron donor.[1−3] Interaction between the $TiCl_4$ catalyst and the $MgCl_2$ support is assumed to be possible because of the similarity of the crystal structures of $TiCl_3$ and $MgCl_2$ and because the ionic radius of Ti^{4+} (68 pm) is nearly the same as that of Mg^{2+} (65 pm).[3] $MgCl_2$ can therefore act as a suitable support material for the $TiCl_4$ catalyst. Before the $TiCl_4$ catalyst can efficiently coordinate to the surface of the $MgCl_2$ support, however, the support material must be activated with internal electron donors that increase its surface area.[4−8]

Traditionally, activation has been achieved by ball-milling of anhydrous $MgCl_2$ with organic electron donors (ketones or esters). Alternatively, the activation can be effected chemically through recrystallization. In this method the anhydrous $MgCl_2$ is dissolved in ethanol, and then other electron donors (ketones or esters) are introduced to the solution. The solution is emulsified in decane by vigorous stirring of the mixture, and ethanol is evaporated in vacuum to recrystallize $MgCl_2$.

The activated $MgCl_2$ support contains the electron donors used as internal donors and any residual ethanol not completely removed in the evaporation. The different electron donors, coordinated to the $MgCl_2$ support, probably have several roles in stereospecific polymerization, but exactly what these roles are is not well understood. It is assumed, however, that the capability of the electron donors to affect the activity and stereospecificity of the catalyst depends on their structural and electronic properties.

The effect of electron donor (ethyl benzoate) on the $MgCl_2$ support has been investigated theoretically with the extended Hückel method.[9] The investigation showed that the electron donor can coordinate to the (100) or (110) surface of $MgCl_2$, whereas the catalyst ($TiCl_4$) preferably coordinates to the surfaces with no electron donors.

In the present work the significance of various electron donors in the modification of the support material was examined by using ab initio calculations. A Mg_5Cl_{10} cluster[10] cut from the (101) surface of $MgCl_2$ provided the surface model. The coordination of alcohols, ketones, esters, and their model compounds to the various coordinatively unsaturated magnesium sites of the $MgCl_2$ support was studied.

2. Computational Methods

The ab initio calculations were carried out with the Gaussian 92 computer program[11] at the restricted Hartree−Fock level of theory with 3-21G, 6-31G, and 6-31G* basis sets. All models investigated were partially geometry optimized: geometrical parameters of the electron donors were fully optimized, while geometrical parameters of the support model were fixed to those in the real crystal structure[12] of $MgCl_2$. In this way, the difficulties associated with the relaxation of a small support model were avoided. If the lattice relaxation effects are to be taken into account, the ab initio techniques with lattice model potential have to be used.[13−15]

The stability of the support−donor complexes was estimated by examining interaction energies defined by comparing the total energy of the complex with the total energies of the separated components. The dependence of these interaction energies on the order of the basis set superposition error (BSSE) was calculated by the counterpoise method.[16,17]

In the coordination of ethanol, acetone, and ethyl formate to the support surface, the electrostatic effect of solvent was taken into account by applying the self-consistent reaction field (SCRF) method.[18−20] In this method the ethanol, acetone and ethyl formate solvent are represented by their dielectric constants. The solute occupies a spherical cavity of radius a_0 within the solvent. The permanent dipole of the solute induces a dipole in the solvent, which in turn interacts with the molecular dipole leading to net stabilization. In the molecular orbital (MO) theory the electrostatic solvent effect is treated as an additional term of the Hamiltonian of the isolated molecule.

3. Results and Discussion

On the basis of previous studies,[21,22] we assume that electron donors, in the same way as the catalyst, coordinate to surfaces of $MgCl_2$ where the coordination sphere of the magnesium atoms is not fully occupied. Such surfaces are the (100), (101),

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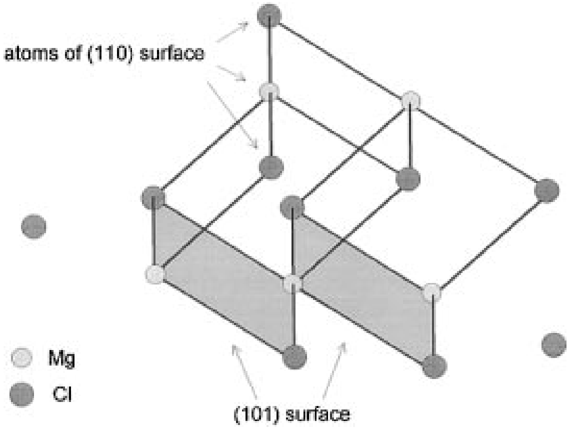

Figure 1. The neutral Mg_5Cl_{10} support model.

(104), and (110) planes. On the (100) surface the magnesium atoms are either three-, five-, or six-coordinated. After reconstruction of the (100) surface, however, the magnesium atoms are most likely to be five-coordinated.[22] The magnesium atoms are also five-coordinated on the (101) and (104) surfaces. The (104) surface is atomically flat, as is the (110) surface where the magnesium atoms are four-coordinated.

As noted above, it can be assumed that in the activation of the $MgCl_2$ support the electron donors coordinate to surfaces where the magnesium atoms have vacant coordination sites. We chose the (110) and (101) surfaces with four- and five-coordinated magnesium atoms as typical examples of such surfaces. The coordination sphere of the magnesium atoms on the (101) surface is similar to that of the five-coordinated magnesium atoms on the (100) surface. However, since it is easier to form a neutral surface model from the inherently stable (101) surface than from the less stable (100) and (104) surfaces,[22] we chose to cut our support model, a neutral Mg_5Cl_{10} cluster[10] (Figure 1), from the (101) surface.

The Mg_5Cl_{10} cluster, which consists of a surface magnesium atom and its nearest-neighbor atoms, contains three types of magnesium atoms: one five-coordinated, two four-coordinated, and two three-coordinated. Thus, with this model we could study the coordination of the electron donors to both four- and five-coordinated magnesium atoms and compare the stability of the electron donors on the (110) and (101) surfaces. The dependence of the electron donor coordination geometry on the number (one or two) of the electron donors coordinated to the same magnesium atom on the (110) surface was also studied. The influence of the support model on the results was not tested, however, because our earlier study[23] showed that the coordination geometry of the catalyst on the support surface is not significantly dependent on the structure of the support model.

3.1. Alcohols. In the first part of the study we investigated the coordination of alcohol compounds to the four- and five-coordinated magnesium atoms of the $MgCl_2$ surface. Water (H_2O), methanol (CH_3OH), and ethanol (CH_3CH_2OH) were the electron donors studied. The water molecule is the smallest model compound that can be used to study the coordination of alcohols to the $MgCl_2$ surface, while the ethanol molecule is the smallest alcohol that could be used as real electron donor in the catalysis.

Examination of the interaction energies (Tables 11 and 3) indicates that the alcohols form very stable complexes with the Mg_5Cl_{10} cluster. However, the estimation of the binding strength depends on the superposition effects, which are 23−30% of the interaction energy with the 3-21G basis set, 11% with the 6-31G basis set, and 12−13% with the 6-31G* basis set. Based on these results, the effect of the BSSE correction on the interaction energies is significant.

TABLE 1: Interaction Energies (ΔE) and Interaction Energies Corrected for BSSE (ΔE(BSSE)) When the Electron Donors Coordinate to the Four-Coordinated Magnesium Atom on the (110) Surface

	basis set	ΔE (kJ/mol)		ΔE(BSSE) (kJ/mol)	
		$n = 1$	$n = 2$	$n = 1$	$n = 2$
$Mg_5Cl_{10}-(H_2O)_n$	3-21G	−262.0	−477.9	−200.7	−335.5
		−322.5[a]		−237.8[a]	
	6-31G	−207.5	−359.5	−189.9	−320.4
	6-31G*	−159.1	−271.2	−142.8	−235.4
$Mg_5Cl_{10}-(CH_3OH)_n$	3-21G	−263.4	−474.9	−204.7	−340.0
		−314.8[a]		−231.1[a]	
	6-31G		−367.3		−325.3
	6-31G*		−275.1		−242.0
$Mg_5Cl_{10}-(CH_3CH_2OH)_n$	3-21G	−268.6	−481.7	−207.4	−340.0
		−312.5[a]		−224.4[a]	
	6-31G		−368.2		−329.2
	6-31G*		−276.2		−242.5
$Mg_5Cl_{10}-(HCOH)_n$	3-21G	−229.6	−428.1	−168.9	−305.7
$Mg_5Cl_{10}-(CH_3COH)_n$	3-21G		−456.7		−329.1
$Mg_5Cl_{10}-(CH_3COCH_3)_n$	3-21G	−266.5	−485.3	−196.6	−338.7
		−265.4[a]		−171.7[a]	
$Mg_5Cl_{10}-(HCOOH)_n$	3-21G	−241.1	−447.0	−176.0	−314.2
$Mg_5Cl_{10}-(CH_3COOH)_n$	3-21G		−487.5		−336.1
$Mg_5Cl_{10}-(HCOOCH_3)_n$	3-21G	−252.1	−462.0	−185.8	−325.5
		−285.8[a]		−188.4[a]	
$Mg_5Cl_{10}-(HCOOCH_2CH_3)_n$	3-21G		−467.6		−330.1

[a] The electron donor coordinates to the five-coordinated magnesium atom on the (101) surface.

Like the accuracy of the energy values, the accuracy of the geometrical parameters (Table 2) depends on the basis sets. In this case the basis sets mostly have an effect on the Mg−O and C−O bond lengths. In the coordination of the ethanol molecules to the Mg_5Cl_{10} cluster, the 6-31G* basis set predicts the Mg−O bond lengths to be about 9 pm longer and the C−O bond lengths about 4 pm shorter than those obtained with the 3-21G basis set. Moreover, the Mg−O and C−O bond lengths calculated with the 6-31G* basis set deviate only slightly from the experimental values.[24]

In the next stage of the work, we elected to use the computationally simpler 3-21G basis set, since it predicts all geometrical parameters except the Mg−O and C−O bond lengths nearly as well as the better basis sets. In addition, if the BSSE correction is taken into account, the interaction energies are of the same order as those calculated with the 6-31G basis set (Table 1).

The stability of the alcohols on the Mg_5Cl_{10} cluster depends on the coordination number of the magnesium atom. When alcohols coordinate to the four-coordinated magnesium atom on the (110) surface, the stability of the complexes increases with the steric bulkiness of the alcohol. On the other hand, when the coordination takes place to the five-coordinated magnesium atom on the (101) surface, the small alcohols form the most stable complexes. The complexes on the (101) surface are also more stable than the corresponding complexes on the (110) surface. This can be explained in terms of the hydrogen bonding between the complexed alcohol and a chloride ion of the (101) surface (Figure 2, in which the hydrogen bond is marked with a dashed line). The $O-H\cdots Cl^-$ hydrogen bond lengths of $Mg_5Cl_{10}-H_2O$ and $Mg_5Cl_{10}-ROH$ ($R = CH_3$ or C_2H_5) vary from 213.0 to 220.0 pm, being the shortest for the $Mg_5Cl_{10}-H_2O$ complex, where the O−H bond length is also distinctly longer than in the other complexes.

The coordination angle formed between the donor and the surface depends on the coordination site and on the number of

TABLE 2: Geometrical Parameters for the Mg_5Cl_{10} Cluster with Water, Methanol, and Ethanol When the Electron Donors Coordinate to the Four-Coordinated Magnesium Atom on the (110) Surface

		r(Mg−O) (pm) complexed		r(X−O)[a] (pm)			r(O−H) (ppm)			∠(X−O−H)[a] (deg)			coordination angle (deg) complexed	
					complexed			complexed			complexed			
	donor	$n = 1$	$n = 2$	free	$n = 1$	$n = 2$	free	$n = 1$	$n = 2$	free	$n = 1$	$n = 2$	$n = 1$	$n = 2$
$Mg_5Cl_{10}-(H_2O)_n$	1st[b]	193.87	199.61	96.63	96.87	96.52	96.63	96.94	97.03	107.8	112.5	112.5	89.0	41.7
	2nd[b]		199.89			96.47			97.15			112.4		40.6
$Mg_5Cl_{10}-(CH_3OH)_n$	1st[b]	194.04	199.66	144.09	148.20	146.74	96.58	96.98	97.00	110.3	112.0	113.0	84.1	40.0
	2nd[b]		199.91			146.52			97.13			112.6		39.9
$Mg_5Cl_{10}-(CH_3CH_2OH)_n$	1st[b]	193.62	199.20	144.43	149.22	147.44	96.61	96.99	97.02	110.9	111.7	112.6	85.4	39.8
	2nd[b]		200.00			147.29			97.17			112.0		40.2
	1st[c]		202.59	143.68		146.44	95.05		95.56	113.7		113.7		39.9
	2nd[c]		202.81			146.24			95.66			113.7		40.6
	1st[d]		208.33	140.46		143.16	94.66		95.26	109.6		111.1		42.8
	2nd[d]		208.58			143.06			95.32			111.0		41.3
	exptl[e]		207.0			143.3			70.0			104.9		

[a] X = C, except in H_2O X = H. [b] With the 3-21G basis set. [c] With the 6-31G basis set. [d] With the 6-31G* basis set. [e] $MgCl_2-(CH_3CH_2OH)_6$ crystal in ref 24.

TABLE 3: Geometrical Parameters and Interaction Energies Corrected for BSSE Using the 3-21G Basis Set for the Mg_5Cl_{10} Cluster with Water, Methanol, and Ethanol When the Electron Donors Coordinate to the Five-Coordinated Magnesium Atom on the (101) Surface

	r(Mg−O) (pm) complexed	r(X-O)[a] (pm)		r(O−H) (pm)		∠(X−O−H)[a] (deg)		coordination angle (deg) complexed	ΔE(BSSE) (kJ/mol)
		free	complexed	free	complexed	free	complexed		
$Mg_5Cl_{10}-H_2O$	198.95	96.63	96.39	96.63	102.02	107.8	111.1	74.5	−237.8
$Mg_5Cl_{10}-CH_3OH$	197.81	144.09	146.05	96.58	101.23	110.3	111.5	74.5	−231.1
$Mg_5Cl_{10}-CH_3CH_2OH$	197.65	144.43	147.18	96.61	100.69	110.9	113.4	76.1	−224.4

[a] X=C, except in H_2O X=H.

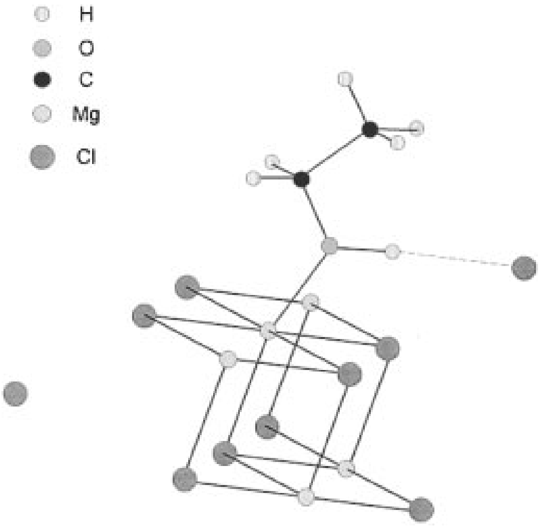

Figure 2. Coordination of ethanol to the five-coordinated magnesium atom.

alcohol molecules. On the (101) surface the magnesium atom has only one vacant coordination site, and for a complete octahedral coordination sphere of the magnesium atom the electron donor is expected to bind perpendicularly to the surface. However, owing to the hydrogen bonding, the coordination angle of the alcohol donors deviates as much as 16° from the rectangular angle (Figure 2).

On the (110) surface the coordination angle (the angle between the Mg−O bond and the surface, marked with the arrow in Figure 3a) is nearly rectangular (84°−89°) in the coordination of one alcohol donor to the magnesium atom. The coordination sphere of the oxygen atom is nearly planar, which is partially due to weak π-bonding between the magnesium atom and the oxygen atom.[25] This type of coordination geometry for the alcohols is energetically so favorable that the energy released in the coordination of a second donor is only two-thirds that of the first donor. The release of energy is less because the coordination angle of the first donor must change from rectangular to about 40° (Figure 4a) in order for the second donor to coordinate to the same magnesium atom. In addition, the possibility for the hydrogen atom of the hydroxy and alkyl group of the alcohols to interact with the chloride ions of the surface is lost on coordination of the second alcohol.

3.2. Ketones. In the second part of the study we investigated the coordination of formaldehyde (HCOH), acetaldehyde (CH_3COH), and acetone (CH_3COCH_3) on the Mg_5Cl_{10} cluster. The formaldehyde and acetaldehyde molecules, which contain the carbonyl group, are the simplest model compounds for ketones, whereas acetone, the smallest ketone, can actually be used as an electron donor in the catalysis. Acetone coordinates to the Mg_5Cl_{10} cluster almost as strongly as the methanol and ethanol donors (Table 1) when the coordination takes place on the four-coordinated magnesium atom. The effect of the BSSE in the acetone complexes is about 26−35% of the interaction energy.

Comparison of the geometrical parameters (Table 4) indicates that, as in the case of alcohols, the structural changes taking place on coordination of the aldehydes and ketones (Table 2) are estimated fairly reliably even with small model compounds. The Mg−O bond length increases whenever two electron donors coordinate instead of one. The C−O and O−H bond lengths in the alcohols and the C−O bond length of the carbonyl group in the aldehydes and ketones are longer in the complexed donor than in the free donor. These parameters are not dependent on the number of the electron donors coordinated to the same four-coordinated magnesium atom.

The coordination angle between the ketone and the four-coordinated magnesium (110) surface is in the range 38.2°−49.0° and, in contrast to the alcohol complexes, is almost independent of the number of electron donors coordinated to the same magnesium atom (Figures 3b and 4b). Owing to the sp^2 hybridization of the carbonyl oxygen, the rectangular coordination angle is not favorable for the ketones on the (110) surface. In the coordination of the ketones to the (101) surface, steric hindrance prevents pure sp^2 hybridization of the oxygen

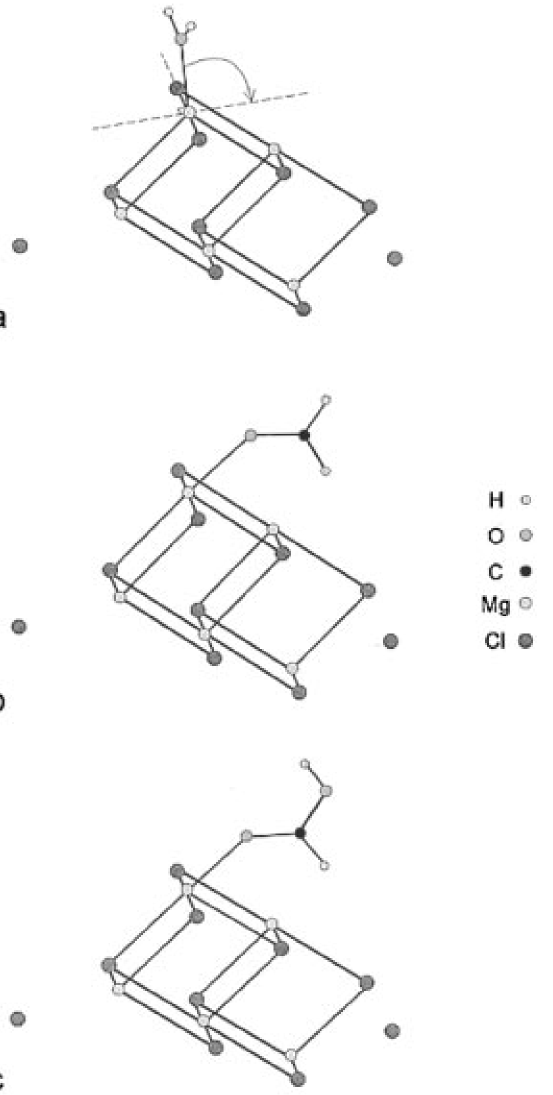

Figure 3. Coordination of one water (a), one formaldehyde (b), and one formic acid (c) molecule to the four-coordinated magnesium atom.

atom, and the stability of the electron donors is not as high on the (101) surface as on the (110) surface.

3.3. Esters. In the third part of the study we investigated the coordination of formic acid (HCOOH), acetic acid (CH_3COOH), methyl formate ($HCOOCH_3$ in Figure 5), and ethyl formate ($HCOOCH_2CH_3$) to the Mg_5Cl_{10} cluster. The carboxylic acids (HCOOH and CH_3COOH) were used as model compounds for the esters ($HCOOCH_3$ and $HCOOCH_2CH_3$). In general, the esters and their model compounds form less stable complexes with the Mg_5Cl_{10} cluster than do the alcohols (Table 1). The effect of the BSSE in these complexes is 29−31% of the interaction energies, but the electrostatic effect of solvent is minor. When the coordination of the ethyl formate to the (110) surface of $MgCl_2$ takes place in ethyl formate solution, the electrostatic effect of the solvent is about 2% of the interaction energy. A similar result was obtained for the coordination of the ethanol in ethanol solution and the coordination of the acetone in acetone solution.

Comparison of the geometrical parameters (Table 5) shows that, as for the alcohol and ketone donors, the structural changes in the ester compounds effected by the coordination can be predicted from the results for the model compounds. The Mg−O bond length increases when two electron donors coordinate instead of one. The $C-O_1$ (O_1 = the oxygen of the carbonyl group) bond length is longer in the complexed donor than in the free donor, while the $C-O_2$ (O_2 = the oxygen of the hydroxy or alkoxy group) bond length is shorter in the complexed donor than in the free donor.

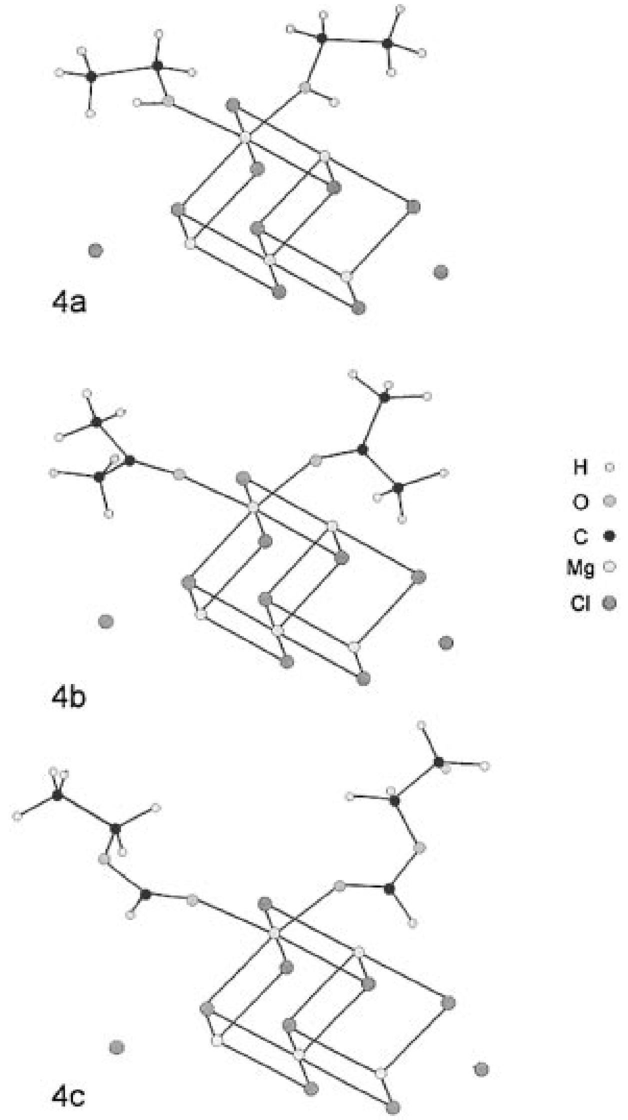

Figure 4. Coordination of two ethanol (a), two acetone (b), and two ethyl formate (c) molecules to the four-coordinated magnesium atom.

As in the case of the ketones, the coordination angle between the ester donors and the four-coordinated magnesium surface is independent of the number of electron donors coordinated to the same magnesium atom (Figures 3c and 4c). Also, the stability of the ester complexes is of the same order as that of the ketones.

Further, the stability of the esters on the Mg_5Cl_{10} cluster does not depend much on the magnesium surface sites, since the interaction energies on the (101) and (110) surfaces differ only slightly from each other in the single electron donor coordination. Owing to the more flexible structure of the esters, the rectangular coordination angle is more favorable for the esters on the (101) surface than for the ketones on the same surface.

3.4. Electron Donors in the Formation of the Catalyst. Some conclusions about the role of the electron donors in the formation of the catalyst can now be suggested. In the activation of $MgCl_2$ the internal electron donors (ketones or esters) coordinate to the vacant sites of $MgCl_2$, as does the residual alcohol. On the (101) surface, the electron donor coordinated to the five-coordinated magnesium atom will probably be the alcohol because, owing to the hydrogen bonding, alcohols form

TABLE 4: Geometrical Parameters Using the 3-21G Basis Set for the Mg_5Cl_{10} Cluster with Formaldehyde, Acetaldehyde, and Acetone When the Electron Donors Coordinate to the Four-Coordinated Magnesium Atom on the (110) Surface

		r(Mg−O) (pm) complexed		r(C−O) (pm)			r(C−X)[a] (pm)			∠(X−C−Y)[a,b] (deg)			coordination angle (deg) complexed	
					complexed			complexed			complexed			
	donor	$n = 1$	$n = 2$	free	$n = 1$	$n = 2$	free	$n = 1$	$n = 2$	free	$n = 1$	$n = 2$	$n = 1$	$n = 2$
$Mg_5Cl_{10}-(HCOH)_n$	1st	198.38	201.80	120.69	123.26	122.84	108.32	107.87	107.75	114.9	118.7	118.4	43.1	38.7
	2nd		201.89			123.05			107.82			118.4		38.3
$Mg_5Cl_{10}-(CH_3COH)_n$	1st		200.47	120.84		123.39	150.69		148.68	114.3		117.3		38.5
	2nd		200.56			123.61			148.63			117.3		38.2
$Mg_5Cl_{10}-(CH_3COCH_3)_n$	1st	193.21	198.10	121.10	124.40	123.81	151.50	149.84	150.11	115.1	117.5	117.1	49.0	39.1
		192.05[c]			123.62[c]			149.61[c]			117.5[c]		85.4[c]	
	2nd		198.38			124.04			150.07			117.1		38.4

[a] X = C, except in HCOH X = H. [b] Y = H, except in CH_3COCH_3 Y = C. [c] The electron donor coordinates to the five-coordinated magnesium atom on the (101) surface.

TABLE 5: Geometrical Parameters Using the 3-21G Basis Set for the Mg_5Cl_{10} Cluster with Formic Acid, Acetic Acid, Methyl Formate, and Ethyl Formate When the Electron Donors Coordinate to the Four-coordinated Magnesium Atom on the (110) Surface

		r(Mg−O$_1$) (pm) complexed		r(C−O$_1$) (pm)			r(C−O$_2$) (pm)			∠(X−C−O$_2$)[a] (deg)			coordination angle (deg) complexed	
					complexed			complexed			complexed			
	donor	$n = 1$	$n = 2$	free	$n = 1$	$n = 2$	free	$n = 1$	$n = 2$	free	$n = 1$	$n = 2$	$n = 1$	$n = 2$
$Mg_5Cl_{10}-(HCOOH)_n$	1st	195.38	199.36	119.77	123.61	123.05	135.02	130.41	131.05	109.5	113.7	113.4	45.3	38.6
	2nd		199.54			123.27			131.06			113.5		38.2
$Mg_5Cl_{10}-(CH_3COOH)_n$	1st		197.68	120.16		123.73	136.01		132.50	110.5		114.1		38.5
	2nd		197.95			123.99			132.62			114.1		38.2
$Mg_5Cl_{10}-(HCOOCH_3)_n$	1st	193.91	198.57	120.00	124.07	123.44	134.35	129.35	130.17	109.9	114.1	113.7	47.6	38.7
		193.34[b]			123.12[b]			132.33[b]			117.1[b]		81.7[b]	
	2nd		198.89			123.64			130.21			113.8		38.4
$Mg_5Cl_{10}-(HCOOCH_2CH_3)_n$	1st		198.34	120.06		123.55	134.23		130.00	110.1		113.7		38.7
	2nd		198.71			123.74			130.05			113.8		38.4

[a] X = H, except in CH_3COOH X = C. [b] The electron donor coordinates to the five-coordinated magnesium atom on the (101) surface.

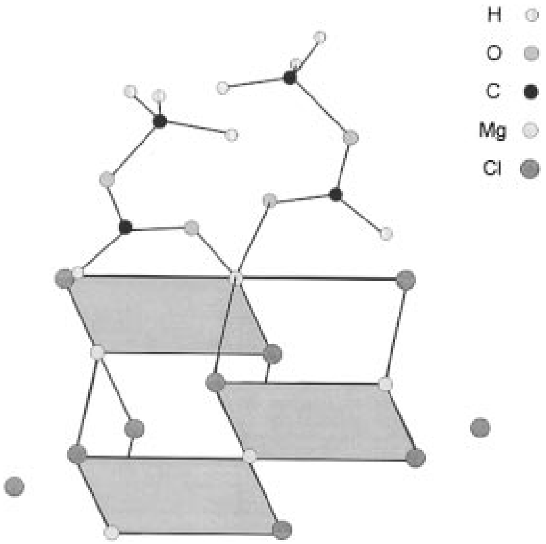

Figure 5. Coordination of two methyl formate molecules to the four-coordinated magnesium atom.

more stable complexes than do the ketones and esters. The situation is less straightforward on the (110) surface, where the stability of the alcohol complexes is reduced by the lack of hydrogen bonding. Here, the alcohol donor has to compete for the vacant sites with the ketones and esters. If a ketone or ester coordinates to the four-coordinated magnesium atom, it is very probable that a second ketone or ester will coordinate to the same magnesium atom. In the case of the alcohol donor the coordination of a second donor molecule is less probable because the coordination angle of the first alcohol donor must change before the second can be coordinated. Therefore, $TiCl_4$ will relatively easily remove the singly coordinated alcohol donors, forming titanium chloride alkoxide,[8] and after this the remaining $TiCl_4$ can coordinate to the (110) surface of $MgCl_2$,[23] forming stereospecific supported catalyst.

4. Conclusions

Study of the interaction between the Mg_5Cl_{10} cluster and the electron donors has shown that the alcohols preferably coordinate to the (101) surface rather than to the (110) surface, owing to the hydrogen bonding. The esters also favor coordination to the five-coordinated magnesium atoms, whereas the ketones preferably coordinate to the four-coordinated magnesium atoms. The coordination geometries of the ketones and esters do not depend on the number of electron donors on the same magnesium atom, unlike the situation for the alcohols. In the coordination of two alcohol donors the coordination angle between the $MgCl_2$ surface and the donor is about 41°, but one alcohol donor coordinates nearly perpendicularly to the surface. This means that a bulky alcohol might even prevent the coordination of a second donor to the same magnesium atom.

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