

Full Paper: This work examines a polymerisation catalyst based on zirconocene with methylaluminoxane (MAO) as a cocatalyst on silica surfaces. Calculations were carried out using the Atom Superposition and Electron Delocalisation method (ASED-MO) considering the (111) and (100) silica planes, both completely and partially hydrated. Our results suggest the production of a cationic

zirconocene as a final step for the active site formation for (111) silica plane, occurring preferentially on partially hydrated silica. On the contrary this may not be possible for the (100) plane, resulting in this case in the formation of a MAO-zirconocene complex as a final and most stable state.

Zirconocene interaction with MAO on (111) and (100) silica surfaces

Alfredo Juan,*¹ Daniel Damiani,² Carolina Pistonesi¹

¹ Departamento de Física, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina
cajuan@criba.edu.ar

² PLAPIQUI, CRIBABB, C. Carrindanga, 8000 Bahía Blanca, Argentina

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1. Introduction

Catalysts based on transition metals are used extensively in the chemical industry for α -olefins polymerisation. Specifically polypropylene is produced currently with heterogeneous Ziegler Natta catalysts based on a compound of a transition metal such as Ti, Zr, or V not supported or supported on MgCl_2 and/or SiO_2 , with a cocatalyst based on Al alkyls. This combination generates a highly active catalyst and high stereospecificity when electron donors are added to the basic formulation.^[1,2]

Metallocenes in combination with methylaluminoxane as cocatalyst form extremely active catalysts for olefin polymerisation. The discovery in 1984 of the isospecific polymerisation of olefins with homogeneous catalysts based in chiral metallocenes of group 4A (ansa metallocenes) and MAO originated a growing experimental and theoretical investigation in this topic.^[3,4] These catalysts polymerise not only with greater activity in homopolymerisation, but also they have the potential to produce new types of polyolefins.^[4,5]

In this work the cluster approximation has been used within the (ASED-MO) theory. We study the adsorption of zirconocene on a model cluster of silica surfaces and the effect of a local model of MAO in the zirconocene adsorption in order to clarify their catalytic performance.

2. Computational method

The calculations were carried out using the Atom Superposition and Electron Delocalisation Molecular Orbital

(ASED-MO) formalism.^[6] The ASED-MO is a semiempirical method, which makes a reasonable prediction of molecular and electronic structures.

This theory is based on a physical model of molecular and solid electronic charge density distribution function, where the last is partitioned in two parts; the atomic charge densities centred on the nucleus and a correction term due to the electronic charge density redistribution that takes place as the atoms come together.^[6,7] The atomic charge densities are easily evaluated using Slater atomic orbital functions. The correction term gives rise to an attractive energy, which can be estimated using an Extended Hückel (EH)-like Hamiltonian.^[8] The diagonal elements of this Hamiltonian are taken as the negative valence orbital ionisation potentials (IP), the off-diagonal elements on the same centre are zero, and the off-diagonal elements on different centres are the average of the corresponding diagonal elements multiplied by, $(1 + 1.25 e^{-0.35R}) S_{ij}$, where S_{ij} is the corresponding valence orbital overlap integral and R is the internuclear distance^[7]. This multiplicative factor can be considered to give an improvement in the EH Hamiltonian in comparison with the Wolfsberg-Helmholtz formulation.^[9] We choose these parameters as suggested by Calzaferri et al.,^[10] and the Slater exponent reported by Bleam and Hoffmann.^[11]

Regarding the atomic basic set, a full valence s + p + d set of the Slater type for valence electron was employed. All these parameters are listed in Tab. 1.

The adiabatic total energy values were calculated as the difference between the energy of the system when the

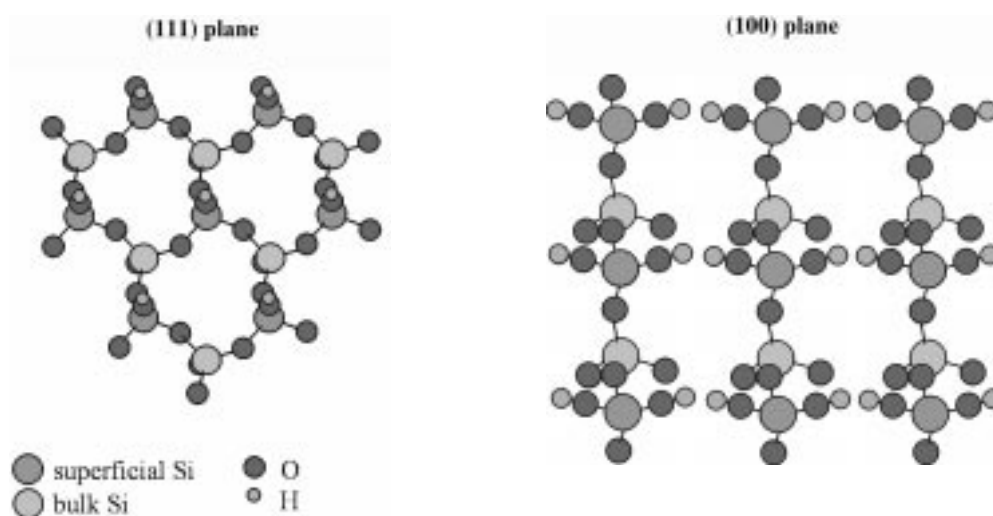


Fig. 1. Surface model (β cristobalite (111) and (100)) showing the arrangement of surface hydroxyls, surface, and bulk silicon atoms

Tab. 1. Atomic parameters

Atom	Orbital	H_{ii}/eV	ζ_1	c_1	ζ_2	c_2
H	1s	-13.60	1.3000			
C	2s	-16.59	1.5536			
	2p	-11.26	1.4508			
O	2s	-32.30	2.2750			
	2p	-14.80	2.2750			
Al	3s	-12.30	1.1670			
	3p	-6.50	1.1670			
Si	3s	-17.30	1.3830			
	3p	-9.20	1.3830			
Cl	3s	-26.03	2.3560			
	3p	-14.20	2.0390			
Zr	5s	-9.87	1.8170			
	5p	-6.76	1.7760			
	4d	-11.18	3.8350	0.621	1.505	0.57963

molecular fragment is at a finite distance to the surface, and the same energy when that molecular fragment is far away from the solid surface:

$$\Delta E = E_{\text{fragment/solid surface}} - E_{\text{fragment}} - E_{\text{solid surface}} \quad (1)$$

where each energy term includes the valence electron energy contribution and the coulombic repulsion between the cores (calculated taking into account all pairs). The charges and the overlap population character were calculated using the Mülliken population analysis.^[12]

The results must be interpreted in their *qualitative* sense due to the ASED-MO approximations. This method is particularly suitable for making relative comparisons when d transition metal atoms are included in the system under study. In the following section we will describe the surface model and the geometrical arrangement of the “active” sites.

3. Components of the system

3.1 The support: silica surface

The building block of silica is the SiO_4 tetrahedron with a silicon ion at the central cavity. In amorphous silica, the bulk structure is determined by a random packing of SiO_4 units, which results in a non-periodic structure.^[13]

Many of the properties of silica depend on the chemistry and geometry of its surface. It is now accepted that the surface silicon atoms tend to have a complete tetrahedral configuration and in an aqueous medium their free valences become saturated with hydroxyl groups forming silanol groups ($\equiv\text{Si}-\text{OH}$), named single or isolated; or geminal silanol groups ($>\text{Si}(\text{OH})_2$).^[14] Peri and Hensley^[15] suggested a model based on the (100) face of β -cristobalite in which each surface silicon atom is connected to a geminal group. De Boer and Vleeskens^[16] proposed a model based on the (111) face of β -cristobalite in which each surface silicon atom is connected to a single silanol group. Experimental work suggests the structure that most closely resembles the silica surface is that of the β -cristobalite or similar crystalline phases. Silica surface may contain segments of surface resembling both the (111) and (100) faces of cristobalite.^[17]

Silica samples exposed to high temperatures under vacuum experience a loss in weight corresponding to the evolution of molecular water due to the condensation of adjacent hydroxyl groups to form siloxane bridges ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$).^[15, 17]

We simulate completely hydrated silica considering the (111) and (100) surfaces of the β -cristobalite, including single silanol and geminal groups, respectively, taking into account the non-ideal crystalline structure proposed by O’Keeffe.^[18] Every Si atom completes its tetrahedron

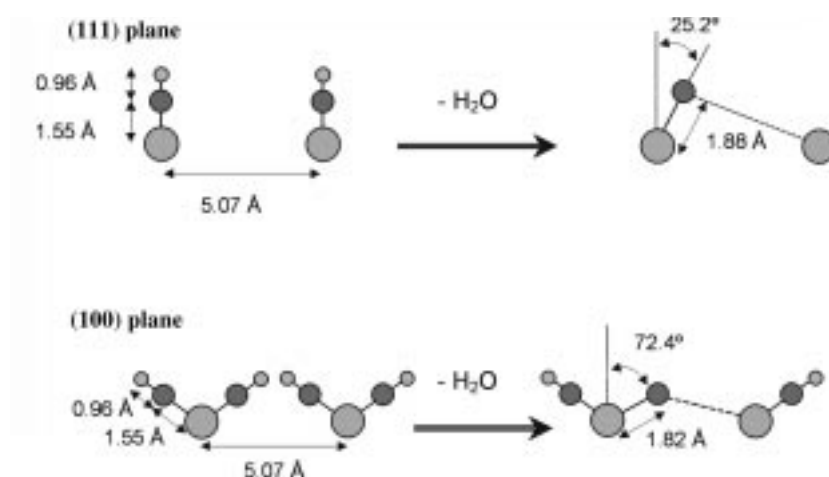


Fig. 2. Polarised siloxane bonds on (111) and (100) silica planes after dehydration

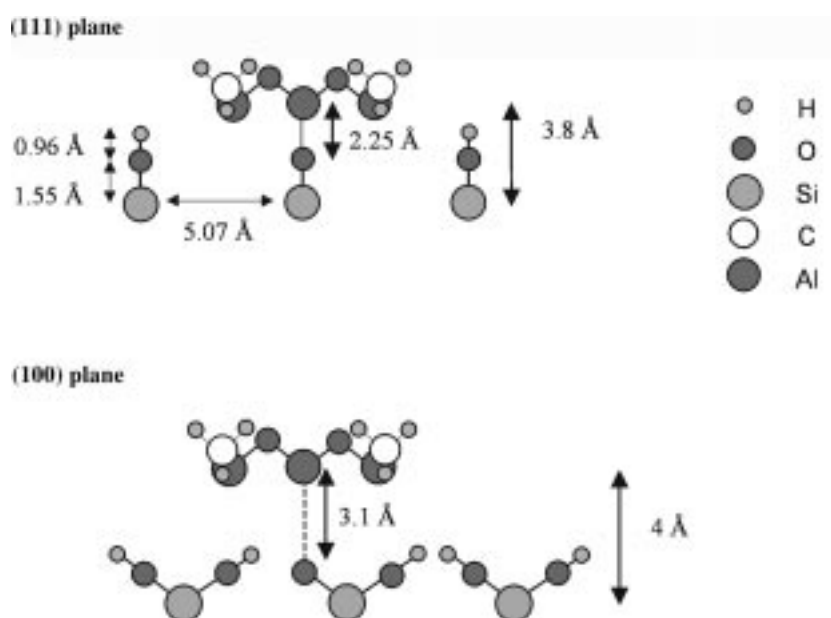


Fig. 3. MAO bonded to (111) and (100) completely hydrated silica surface in the most favourable configuration

with O atoms. We use the following distances: Si—Si 5.07 Å; Si—O (surface) 1.5 Å; O—O (bulk) 2.53 Å; O—H 0.96 Å and H—H 5.07 Å. Part of these clusters are shown in Fig. 1.

Partially hydrated silica was modelled by polarised siloxane bonds on the surface after dehydration,^[19] on (111) and (100) planes. Our calculations suggest distances and angles for polarised siloxane bonds, with the O ion unequally shared as shown in Fig. 2.

For silica supports, the dangling bonds of silicon and oxygen at the back surface often are very successfully singly saturated with H atoms.^[20] In this work the dangling bonds were saturated in that way.

3.2 The cocatalyst: Methylaluminoxane (MAO)

MAO is a compound in which aluminium and oxygen atoms are arranged alternately and free valences are saturated by methyl substituents. Determination of its crystal structure is a very difficult task due to experimental discrepancy and the dependency on the synthetic conditions, isolation methods, solvent used, etc.

Many structures were proposed, like polymeric linear chains, two-dimensional structures and cyclic rings.^[21–23]

The MAO model used in this paper was made considering that the interaction takes place through a H atom belonging to a surface OH group. Interaction is followed by evolution of CH₄ and the formation of a Si—O—Al

bond. Our complete string is $(\text{CH}_3)_2\text{Al}-\text{O}-\text{Al}-\text{O}-\text{Al}(\text{CH}_3)_2$ and it is bonded to the surface through the central Al atom. Al—O and Al—C distances in our MAO are 1.5 Å and C—H distance is 1.1 Å.

Under these conditions, the energy of the MAO/Silica system was evaluated for different MAO locations and orientations. The most favourable configurations for the completely hydrated case are shown in Fig. 3 where the Al (from MAO) —O (from surface) distance was 2.25 Å for the (111) plane and 3.1 Å for the (100) plane. Similar locations were obtained for partially hydrated cases.

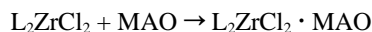
3.3 The catalyst: Zirconocene

The selected zirconocene $\text{EtInd}_2\text{ZrCl}_2$ was modelled in one of the two racemic forms^{24]}. The Zr—Cl bond length was 2.56 Å and the Cl—Zr—Cl angle was 90°.

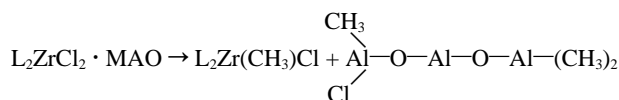
4. Interaction within the components: Active site formation

The mechanism of the active site formation, may consist of the following steps (as proposed by Kaminsky et al.^[25–27])

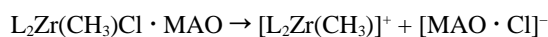
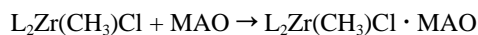
I-Complexation: Metallocene and MAO form a complex



II-Methylation: Following complexation an exchange is produced between a Cl atom from zirconocene and a methyl group from MAO (alkylation)



III-Activation: a rapid dissociation into an ion pair occurs



Both systems are active but the cationic complex (cationic metallocene) is significantly more active.^[26]

Zirconocene adsorption is analysed considering the most stable configuration for the MAO/Silica surface. Zirconocene approaches the surface with Cl—Zr—Cl in the same plane of the Al—O—Al string of MAO. We take the initial state (zirconocene far away from MAO-silica system) as the reference energy value. So the energy change during complexation is calculated according to the equation:

$$\Delta E_{\text{compl}}(\text{L}_2\text{ZrCl}_2) = E(\text{L}_2\text{ZrCl}_2 \cdot \text{MAO/silica}) - E(\text{L}_2\text{ZrCl}_2) - E(\text{MAO/silica}) \quad (2)$$

For the methylation step the energy difference is calculated by:

$$\Delta E_{\text{methyl}} = E(\text{L}_2\text{ZrCl}(\text{CH}_3) \cdot \text{MAO}_{\text{Cl}}/\text{silica}) - E(\text{L}_2\text{ZrCl}_2) - E(\text{MAO/silica}) \quad (3)$$

in which MAO_{Cl} means a MAO molecule with a Cl atom replacing a methyl group. The adsorption energy of $\text{L}_2\text{ZrCl}(\text{CH}_3)$ can also be calculated as

$$E_{\text{ads}}(\text{L}_2\text{ZrCl}(\text{CH}_3)) = E(\text{L}_2\text{ZrCl}(\text{CH}_3) \cdot \text{MAO}_{\text{Cl}}/\text{silica}) - E(\text{L}_2\text{ZrCl}(\text{CH}_3)) - E(\text{MAO}_{\text{Cl}}/\text{silica}) \quad (4)$$

Previous to activation, it was considered that the $\text{L}_2\text{ZrCl}(\text{CH}_3)$ molecule interacts with a new and complete MAO molecule, without Cl (we call this refresh). Now the adsorption energy is:

$$E_{\text{ads}}(\text{L}_2\text{ZrCl}(\text{CH}_3)) = E(\text{L}_2\text{ZrCl}(\text{CH}_3) \cdot \text{MAO/silica}) - E(\text{L}_2\text{ZrCl}(\text{CH}_3)) - E(\text{MAO/silica}) \quad (5)$$

Next, the cationic zirconocene is generated^{28, 29]} removing a Cl atom from zirconocene, and moving it towards a Si atom (near MAO), with its OH group previously removed and the energy difference between final state (Cl atom not bonded to zirconocene) and initial state (Cl bonded to zirconocene) is calculated.

5. Results

5.1 Complexation and methylation

MAO-Zirconocene interaction was analysed considering (111) and (100) silica planes both completely and partially hydrated. The energy values and distances obtained are shown on Tab. 2.

Orientations and localisations are similar on partially and completely hydrated silica when referring to the same plane; Fig. 4 shows these configurations.

The energy values obtained for complexation suggest that the methylation process involves a decrease in the energy of the system, meaning a favourable step for all the cases under consideration. This means that when MAO and zirconocene approach, they form a complex.

Considering the (111) plane, complexation is 10 eV stabilised when the surface is dehydrated. On the other hand, on the (100) plane, the degree of hydration is not

Tab. 2. Complexation and methylation results

	$\Delta E_{\text{compl}}/\text{eV}$	Cl—(Al—Al—Al) dist./Å	$\Delta E_{\text{methyl}}/\text{eV}$
(111) hydrated	−20.90	4.6	−23.50
(111) part. hydrated	−30.72	4.6	−34.47
(100) hydrated	−77.00	2	−73.19
(100) part. hydrated	−77.03	2	−73.22

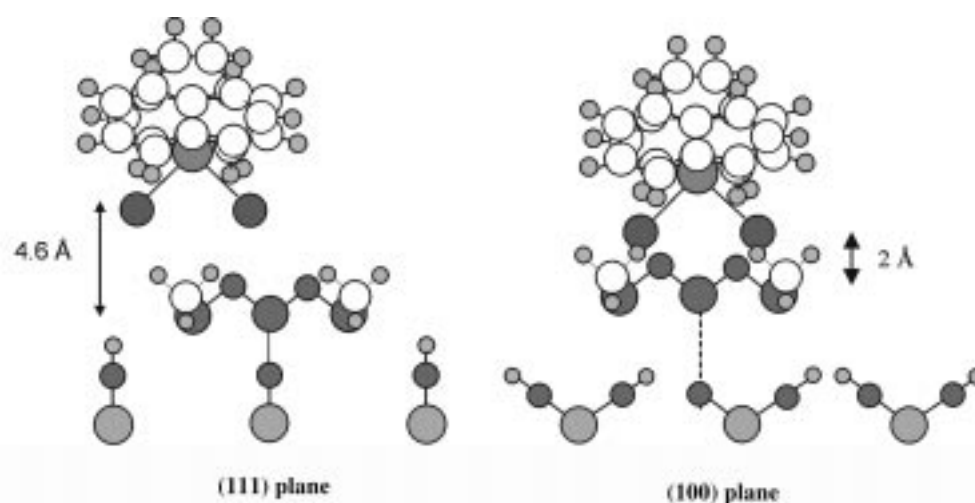


Fig. 4. The most favourable location for zirconocene on a MAO/silica system

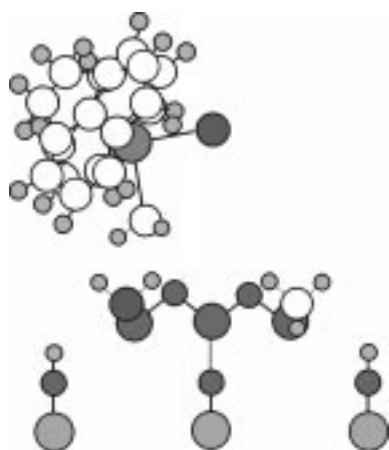


Fig. 5. The most stable configuration when the exchange between Cl and a methyl group is produced during methylation (for (111) completely hydrated)

very significant to the energy value. But the binding to the surface is much stronger when compared with the (111) surface. Also zirconocene and MAO are much closer together, as shown in Fig. 4.

During the methylation step, a possible exchange between a Cl atom from zirconocene and a methyl group from MAO is also computed. Beginning with the previous configuration (resulting from complexation), simplified ways in which this exchange could be produced were analysed. After testing different locations and orientations of the $L_2ZrCl(CH_3)$ molecule, the lower energy values obtained are shown in Tab. 2. In all cases there is a preference for methyl group (now in zirconocene) to be closer to the MAO, as shown for (111) completely hydrated in Fig. 5.

In this case and in the previous step, the same reference energy value was considered. Considering the (111)

plane, this means that the methylation process involves a decrease in the energy of the system, meaning a favourable step. The system is stabilised by 2.6 eV for the completely hydrated case, and by 3.77 eV for the partially hydrated one.

For the (100) plane, the results in Tab. 2 show that methylation process would imply an increase in energy value. These values both for the partially and completely hydrated case, mean an increase in the energy of the system, relative to the complexation step.

So for this case methylation is an energetically unfavourable step, because it would involve an increase in energy of 3.81 eV (a barrier impossible to overcome, even considering thermal fluctuations). So the following steps are not considered for the (100) plane.

5.2 Activation

In the first part of this step, the methylated zirconocene is adsorbed on a refreshed MAO. In Tab. 3 the $L_2ZrCl(CH_3)$ adsorption energy during refresh and also for the previous (methylation) step is shown. So adsorption on refreshed MAO is in both cases more stable than the previous to activation step.

Next, the cationic zirconocene has to be generated. One possibility is that a Cl atom from zirconocene is bonded to a Si atom (near MAO), with its OH group previously removed. In order to carry that out, different Si atoms close to MAO were considered.

Tab. 3. Adsorption energy for $L_2ZrCl(CH_3)$ on MAO_{Cl} and on refreshed MAO

E_{ads}/eV	Completely hydrated	Partially hydrated
$L_2ZrCl(CH_3)/MAO_{Cl}/silica$	-5.38	-14.53
$L_2ZrCl(CH_3)/MAO/silica$	-6.20	-15.94

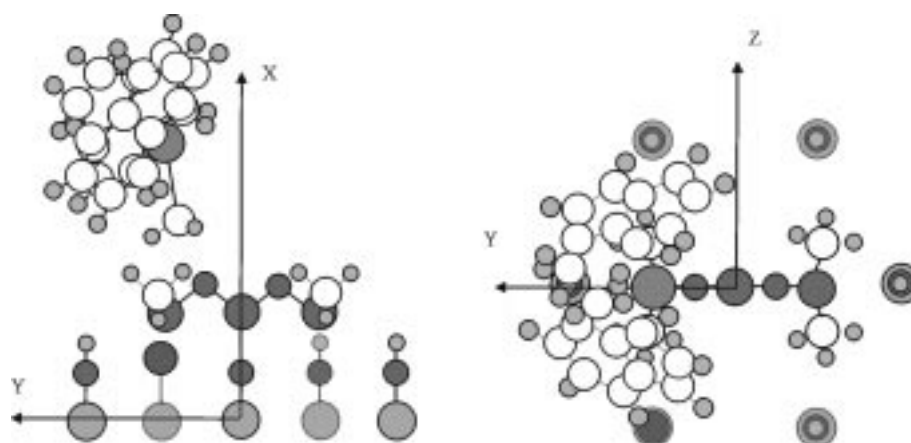


Fig. 6. Cationic metallocene and its orientation for (111) completely hydrated silica plane (atoms not in the Al—O—Al—O—Al plane are indicated by dashed lines)

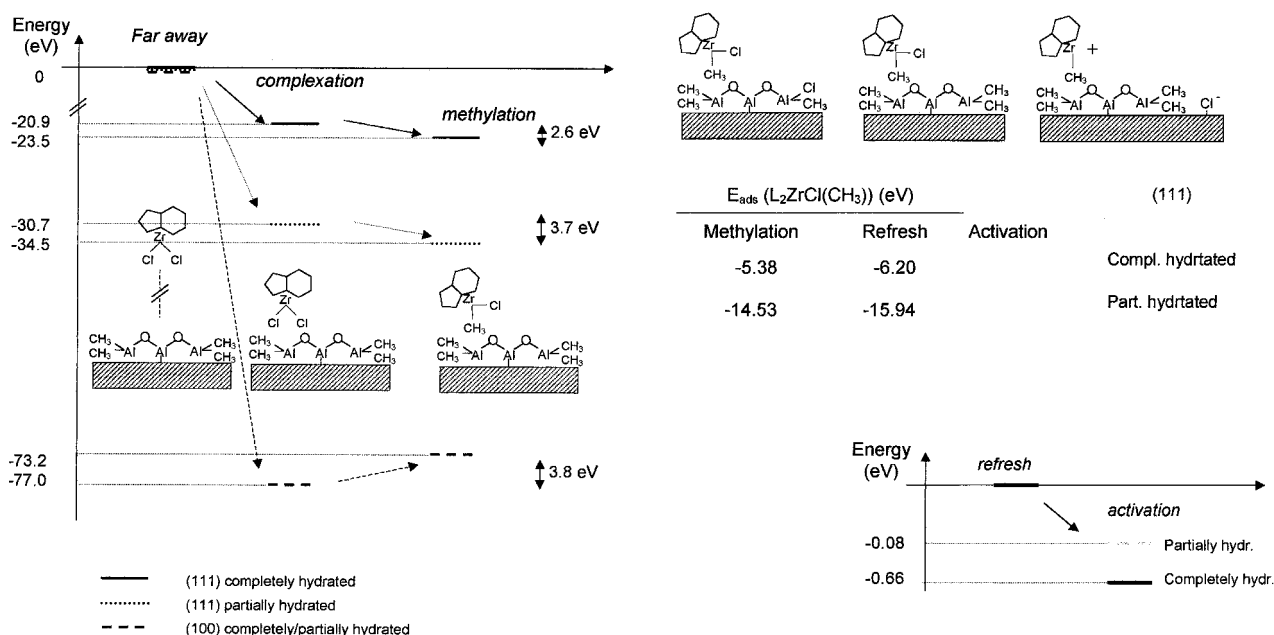


Fig. 7. (a) Energy steps for all cases studied before methylation; (b) Energy steps from methylation to activation

In all cases the Cl atom was moved towards a Si atom and the energy difference between the final state (Cl atom not bonded to zirconocene) and initial state (Cl bonded to zirconocene) was calculated. In all cases a Cl—Si bond is obtained, which is of course energetically favourable (the energy of the system diminishes when Cl is removed from zirconocene and a cationic zirconocene is obtained). The most favourable orientation is obtained when the Cl atom is bonded to a lateral Si atom as shown in Fig. 6 for (111) completely hydrated. The energy is reduced by 0.66 when the Cl—Si distance is 1.85 Å for the completely hydrated case and by 0.08 eV and the same Cl—Si distance for the partially hydrated case.

To justify the procedure of the cationic zirconocene formation, the adsorption energy of the Cl bonded to a Si

(without its OH) and the adsorption energy for an OH group were evaluated. The adsorption energy for the OH was -3.08 eV while for Cl it was -6.80 eV. This means that a Cl atom could replace an OH on the silica surface.

All the results in this section are summarised in Fig. 7a and 7b (the scale is qualitative).

6. Conclusions

Our model suggests that MAO and zirconocene may form a complex, which is more strongly bonded for the (100) silica plane.

A methylation process may be possible when referring to the (111) silica plane, being more favourable for the partially hydrated case.

For the completely and partially hydrated (111) plane, the methylated zirconocene is strongly adsorbed on a “fresh” and complete MAO when compared with a MAO where one Cl replaces a methyl group. In both cases the formation of a cationic zirconocene is an energetically favourable step.

Energies involved in the whole process are almost 10 eV lower in the partially hydrated case, than in the totally hydrated one. This suggests that this process may occur preferentially over partially hydrated silica.

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