A semi-empirical study on Ziegler Natta catalyst: Concerning the interaction $EtInd_2ZrCl_2/MAO/SiO_2$

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Abstract

A modified extended Hückel method (EHMO), which includes core–core repulsion terms, was used to study a propylene polymerization heterogeneous catalyst by modeling the adsorption of the ansa-metallocene ethylen-bisindenylzirconium dichloride ($C_2H_5(C_9H_6)_2ZrCl_2$ from now on $EtInd_2ZrCl_2$) on SiO_2 surfaces. The adsorption was considered to occur at two faces of SiO_2 (with geminal and isolated OH's) and at two different temperatures for SiO_2 pretreatment (200 and 600°C). Taking into account that the interaction with Al compounds is considered as a way to improve the catalyst performance, specially with methylaluminoxane (MAO), a local model of aluminoxane (AlO) was added to Si–O bond with the subsequent metallocene adsorption. The results show that AlO improves the zirconocene adsorption on SiO_2 modeled at 200°C while it inhibits that process at 600°C.

Keywords: Metallocene supported catalysts; Molecular orbital

1. Introduction

At present, the production of isotactic polypropylene is based on the use of complex heterogeneous catalysts. Since the discovery of the isotactic polymerization with chiral ansa metallocenes such as ethylen-bisindenyl zirconium dichloride $(C_2H_5(C_9H_6)_2ZrCl_2$ or $EtInd_2ZrCl_2)//$(methylaluminoxane) MAO [1],

much effort has been devoted to modify the metallocene catalysts for practical use. Chien et al. have reported that zirconocene catalysts supported on SiO_2 show activities comparable to homogeneous catalysts [2]. Kaminsky et al. have obtained highly isotactic polypropylene (PP) using the SiO_2 supported metallocene catalysts prepared by a unique method combined with MAO [3]. Soga et al. [4] have developed a highly isospecific SiO_2 supported zirconocene catalysts activated with ordinary aluminum alkyls compounds. Metallocene supported on different silicas, prepared from chemically modified silica gel was also used in propylene poly-

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merization. It has been mentioned that the weakly fixed zirconocene could be responsible for the production of PP with low isotacticity [5,6].

Recently, in the open literature several authors have reported theoretical studies on Ziegler Natta olefin polymerization mechanisms focused on ansa-metallocenes [7] and diolefins [8]. Specific topics have been studied by EHMO [9] or through ab-initio methods [10]. But the metallocene catalysts using SiO_2, Al_2O_3 or $MgCl_2$ as support have not been so deeply studied. The effect of the alkylaluminum on the surface and adsorption has not been considered at theoretical level. Some patents claim that $MgCl_2$ is an attractive support for ansa-metallocenes [11]. However SiO_2 is the most widely accepted support to obtain high activity and stereoselectivity in propylene polymerization [12,13] or copolymerization [14]. Some unsolved questions about the relationship between the catalysts preparation conditions and its performance in the propylene polymerization are still present. While similar supports and active materials have been used, strongly different activity results have been reported. We believe that the quality and quantity of surface hydroxyls, resulting from different thermal treatments and the effect of MAO on different surfaces could be responsible for that unusual behavior. The researches cited herein include ab-initio as well as semiempirical methods. However the metallocene adsorption on SiO_2, Al_2O_3 or $MgCl_2$ and the influence of alkyl aluminum compounds have not been considered by a theoretical approach. In the present work the SiO_2 surface was modeled at 200 and 600°C and two different planes were studied: with geminal and isolated OH's. The purpose of this paper is to study the adsorption of an ansa metallocene on a model cluster of SiO_2 and the effect of a local model of MAO (called AlO) in the zirconocene adsorption in order to clarify their catalytic performance. The population of surface OH's, obtained from experiments at both selected temperatures, was also considered.

2. The surface models and the structure of the sites

2.1. The SiO_2 surface

SiO_2 has three forms at atmospheric pressure, stable at a certain range of temperature. Up to 870°C, SiO_2 adopts the quartz structure. After that and up to 1470°C it adopts the tridimite form and from 1470 to 1710°C it can be isolated as cristobalita [15].

A considerable amount of research has been devoted in the past to characterize the surface structure of amorphous silica, particularly by using infrared spectroscopy to identify the different OH species present at the surface. Terminal silicon atoms of the amorphous network can be combined through an oxygen bridge or to hydroxyl radicals, constituting a *siloxane group* ($\equiv$Si–O–Si$\equiv$) or they can form a silanol group ($\equiv$Si–OH). When silanol groups are not linked by a hydrogen bond they are *isolated silanols* (*AIS*). If two silanol groups are bonded to the same silicon atom they are *geminal silanols* (*GEM*) ($>$Si(OH)$_2$). When silica samples are calcined a dehydration process leads to a decrease in the total number of surface hydroxyls and to a variation in the relative proportion of isolated to geminal species. After the removal of physically adsorbed and bulk water (specially for microporous SiO_2) at relatively low temperature ($\approx$ 100°C), heating at higher temperatures produces the condensation of hydroxyl groups of adjacent silicon atoms into water molecules. Beginning with a concentration of $\approx$ 5.8 OH/nm^2 at 100°C this value decreases to $\approx$ 1 OH/nm^2 at 900°C [17]. Several geometrical models have been proposed to account for this complex structural features. They are based on the assumption that the amorphous silica surface can be assimilated to (100) (GEM) and (111) (AIS) patches of β-cristobalita. The first model due to De Boer and Vleeskins considers that silanols groups are arranged in a hexagonal array corresponding to the (111) face of β-

cristobalita [18]. The actual amorphous silica surface cannot be treated simply like a patching of (100) and (111) faces of this crystal due to the important contribution of (100)–(111) borderline, particularly in the case of very small patches. Moreover, no precise information is available regarding the relative proportion of these faces and only the relative fraction of isolated to geminal hydroxyl surface densities is known. So, we considered that to analyze both situations separately is more appropriate, that is, adsorption on the (100) plane and adsorption the (111) plane; specially to avoid the random modeling of hydroxyls on amorphous silica, that cannot reproduce exactly the borderlines of small patches. In the present paper we model the 'pure' forms of both planes. In the real situation, (100) GEM is near 15% of total surface [25]. The distances were obtained by energy minimization. The OH and Si–O–Si surface links have been optimized [25].

It must be emphasized that the ab-initio calculations reported in the literature have been performed on very small clusters simulating different silica rings. *In the last calculations*, due to the amorphous character of this system, the attention was only focused on the local microscopic distribution of hydroxyls. In spite of this morphologic simplification, agreement with thermogravimetric dehydration was reported [25,26]. Moreover, the important adsorbate–surface interactions in metallocene supported catalysts are of short range.

The characteristic distances of the selected structure are collected in Table 1.

2.2. The methylaluminoxane (MAO) model

Some authors (Chien [2] and Soga [4,5]) reported that pretreatment of silica with MAO, before supporting the zirconocene, improves activity and selectivity for propylene polymerization catalysts. An approach to overcome the problem of the costly technology using soluble systems with MAO, the results of which have been mainly disclosed in the patent literature,

Table 1
Distances in (100) GEM and (111) AIS of β-cristobalite

Surface	Distance (Å)
(100)GEM	Si–Si = 5.06
	Si–O = 1.543
	O–O = 2.54
	O–H = 0.968
	H–H = 4.1
(111)AIS	Si–O = 1.55
	O–O (bulk) = 2.54
	O–O (surface) = 5.06
	H–H = 5.06

involves adsorbing an appropriate metallocene, with or without an alkyl aluminum (generally trimethylaluminum-TMA) or MAO. Different results are obtained when the support, SiO_2 is treated either with TMA or MAO. The thermal pretreatment of the support is important, too. When MAO is used, significant amounts of the aluminum compound as well as 60 to 100% of starting zirconocene are retained onto the support. The homogeneous zirconocene and the one supported on SiO_2 modified by MAO produce the same kind of polymer. These authors said that the same metallocene cation-like active species is formed by interaction of metallocene and MAO when MAO is in solution as well as when it is anchored to the silica surface. This is taken as an indication that MAO does not decompose as a consequence of the interaction with the silica surface. The interaction takes place through a H atom belonging to a surface OH. Interaction is accompanied by CH_4 evolution and the formation of a Si–O–Al bond. Therefore, the interaction of MAO with the surface takes place through only one site. When TMA is used to modify the surface, the zirconocene is not decomposed and these systems are not active for propylene polymerization in the absence of aluminoxane or an adequate alkyl aluminum (for example: $AliBu_3$). So, the surface chemistry of the $AlMe_3$-treated supports does not mimic that of methylaluminoxane in generating significant concentrations of active sites. In order to evaluate the effect of Al–O
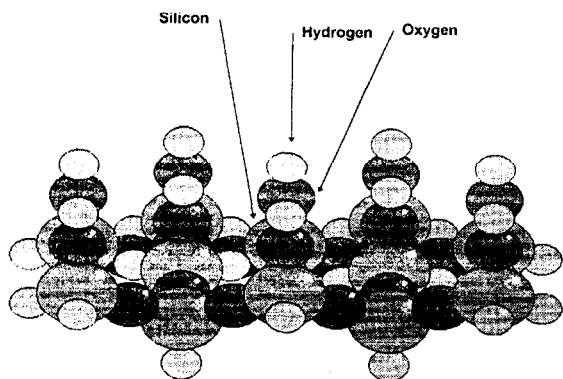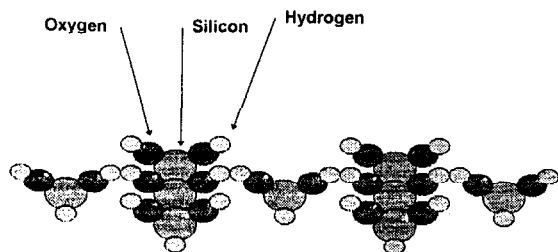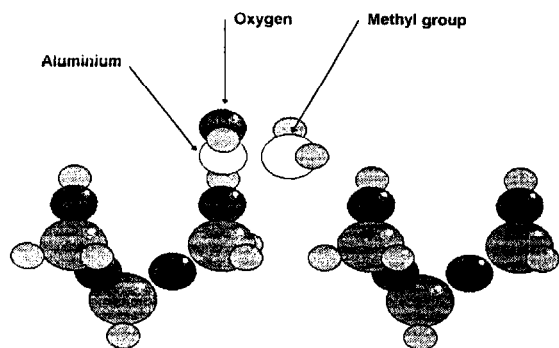
Fig. 1. (111) AIS plane model of β-cristobalita at 200°C.

Fig. 3. (111) AIS plane model of β-cristobalita at 200°C with an AlO group. For clarity the methyl groups were not included.

bonds at the surface, the aluminoxane was *locally* modeled adsorbed on a single surface site through a Si–O–Al bond. MAO is an oligomer of trimethylaluminum and water [(–Al(CH$_3$)O–)$_n$ with $n = 6$–20]. Our proposed model uses a sequence with $n = 3$. The complete string is (CH$_3$)AlH-OAlOAlH(CH$_3$) and it is bonded to the silica surface through the central Al atom. Bond lengths were obtained from specific literature [16]. We called that aluminoxane *AlO group*.

Higher dehydration temperatures were not considered because there are many reports about the negative results of their utilization in catalysts performance. It is usually found in the patent literature that 800°C is the maximum temperature admitted for a good catalyst performance [12–14].

2.3. SiO$_2$ at 200°C

SiO$_2$ was modeled in the following way: with geminal OH ((100) GEM plane) and with isolated OH ((111) AIS plane). Sixty three atoms were used to model the (100) GEM face while 68 were used for the (111) face. In the GEM face, 9 Si, 18 O and 36 H were placed. The (111) AIS face was formed using 14 Si, 22 O and 32 H (see Figs. 1 and 2). In both clusters dangling bonds were saturated with hydrogen atoms.

When the AlO string was considered, 15 additional atoms were added (3 Al, 2 O, 8 H and 2 C) on a surface Si–O bond lacking a H atom [17,18] (see Figs. 3 and 4).

2.4. SiO$_2$ at 600°C

SiO$_2$ was modeled by means of two clusters taking into account the temperature effect. In the case of the (111) AIS plane, 6 OH from silanols groups were condensed producing 3 siloxane groups (see Fig. 5). The surface oxygen atoms were positioned at the same level than Si atoms. In the remaining plane ((100) GEM), two OH from neighboring =Si(OH)$_2$

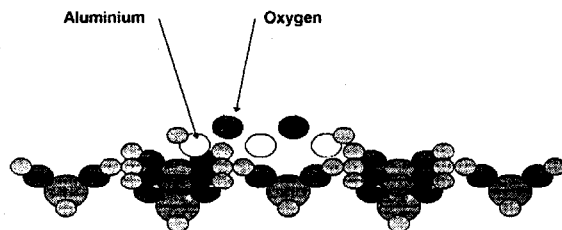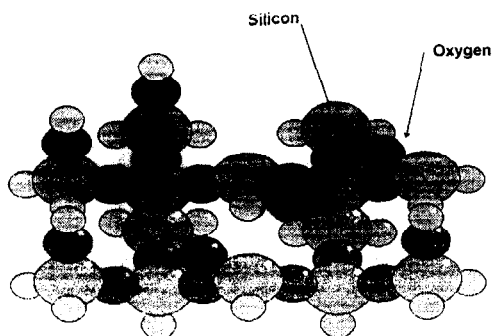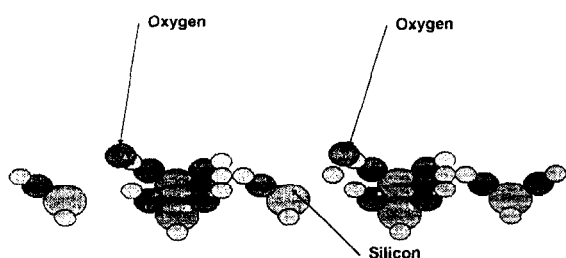Fig. 2. (100) GEM plane model of β-cristobalita at 200°C.

Fig. 4. (100) GEM plane model of β-cristobalita at 200°C with an AlO group. For clarity the methyl groups were not included.
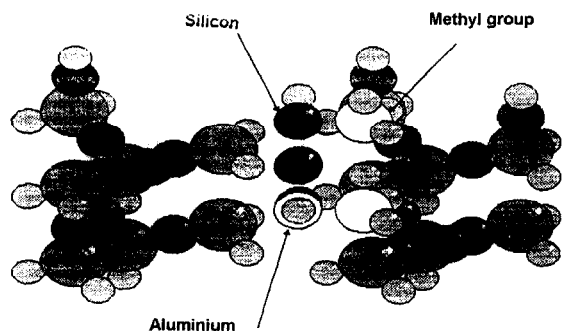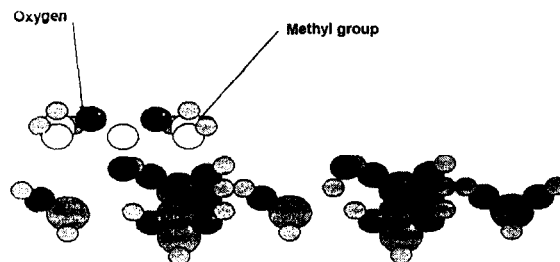
Fig. 5. (111) AIS plane model of β-cristobalita at 600°C.

Fig. 6. (100) GEM plane model of β-cristobalita at 600°C.

react to produce two (OH)Si–O–Si–(OH) groups (see Fig. 6).

When the AlO was considered, 15 additional atoms were added (3 Al, 2 O, 8 H and C) on a surface SiO bond (see Figs. 7 and 8). Distances and bond angles were obtained from literature [16].

2.5. The zirconocene

The selected zirconocene (EtInd$_2$ZrCl$_2$) was modeled in one of two racemic forms [19,20]

Fig. 7. (111) AIS plane model of β-cristobalita at 600°C with an AlO group.

Fig. 8. (100) GEM plane model of β-cristobalita at 600°C with an AlO group.

(see Fig. 9). The Zr–Cl bond length was 2.56 Å and the Cl–Zr–Cl angle was 98.6°. The CR (centroid 1) (1)–Zr–CR (centroid 2) (2) angle was 120°.

2.6. The extended Hückel method (EHMO)

Molecular orbital calculations were carried out by means of the extended Hückel method (EHMO), a semi-empirical procedure which provides a useful preliminary approach to the electronic structure. This formalism has been widely used in the past to study electronic energy changes [21] and it is useful to obtain qualitative trends in adsorption processes [22]. Hence we believe that this method is a better approach to study the active site precursor formed during the impregnation step as an initial screening of potential catalytic materials than the conventional trial and error method.

The program used (ICONC) was developed by Calzaferri et al. [23]. It includes repulsive terms to the total energy which are not explicitly included in the EHMO). The repulsive
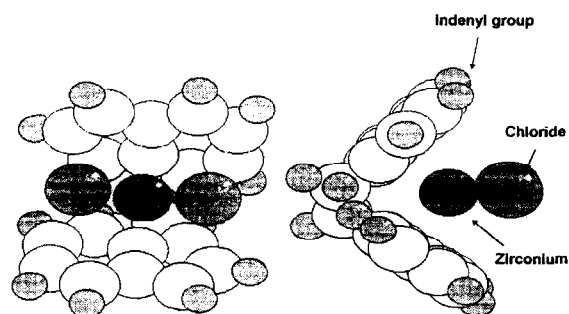

Fig. 9. EtInd$_2$ZrCl$_2$.

Table 2
Atomic parameters used for EHMO calculation

Atom	Orbital	Orbital exponents	Ionization potentials (eV)
H	1s	1.000	−13.60
C	2s	1.154	−19.65
	2p	1.451	−11.13
O	2s	2.163	−31.6
	2p	2.750	−16.78
Al	3s	1.670	−12.30
	3p	1.383	−6.50
Si	3s	1.60	−20.44
	3p	1.60	−12.41
Cl	3s	2.356	−26.03
	3p	2.039	−14.20
Zr	5s	1.817	−9.870
	5p	1.776	−6.760
	4d	3.835 (0.6211)[a]	−11.18
		1.505 (0.5796)[a]	−11.18

[a] Coefficients used in the double ξ expansion of the d orbitals.

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 SiO_2 cluster and the energy of the molecule lying far away from the solid surface. The atomic parameters are listed in Table 2.

3. Results

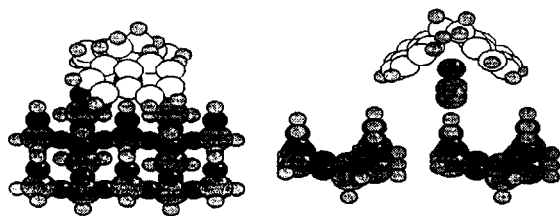One of the most important factors that should be considered in the modeling is the surface

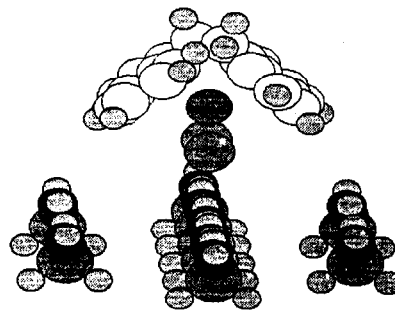Fig. 10. EtInd$_2$ZrCl$_2$ adsorption on (111) AIS plane at 200°C.

Fig. 11. EtInd$_2$ZrCl$_2$ adsorption on (100) GEM plane at 200°C.

structure that the zirconocene 'sees' during the adsorption. In order to make a complete comparison the results will be presented for each plane and temperature.

3.1. SiO_2 at 200°C

3.1.1. Without AlO

The zirconocene approaches to both surfaces (GEM and AIS) at 2 H of surface hydroxyls (see Figs. 10 and 11). The H–H distance is 5.06 Å in the AIS plane and 4.1 Å in the GEM plane. This length of non-bonded interaction is similar to the Cl–Cl non-bonded distance in the zirconocene molecule (3.62 Å) (see Fig. 9).

It can be seen in Fig. 12 that zirconocene adsorption is favored on geminal OH with an energetic minimum at a H–Cl distance 3.1 Å. At the isolated OH's the adsorption is hindered.
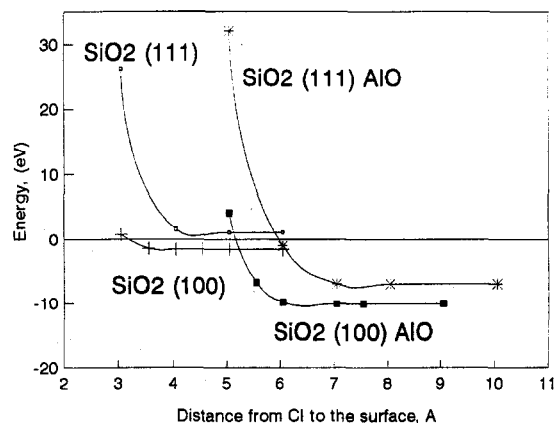

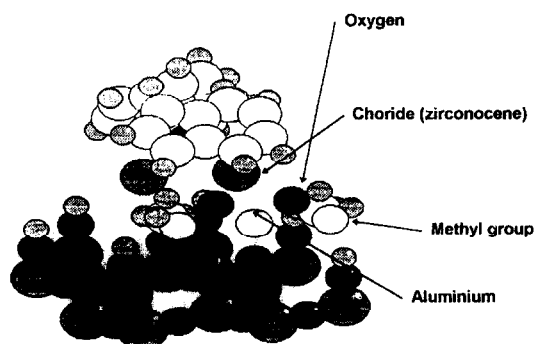Fig. 12. Adsorption energy versus EtInd$_2$ZrCl$_2$-surface distance (at 200°C).

Fig. 13. EtInd$_2$ZrCl$_2$ adsorption on (111) AIS plane at 200°C/AlO.

Fig. 15. EtInd$_2$ZrCl$_2$ adsorption on (111) AIS plane at 600°C.

3.1.2. With AlO

The AlO string on the surface modifies the energy situation presented above. At both planes the adsorption is more stable than in the absence of AlO. The zirconocene approaching to the surface is favored because Al–Al distance is similar to Cl–Cl distance in the zirconocene. The interaction is given between Al and Cl and between O and Zr (see Figs. 13 and 14). It must be mentioned that no appreciable minimum is observed but the species are stable and possible at both planes.

3.2. SiO$_2$ at 600°C

3.2.1. Without AlO

The zirconocene approaches to surface oxygen. When the (111) AIS plane is considered, the adsorbate is placed between 2 surface O (see Fig. 15). In the case of the (100) GEM plane, the metallocene is placed on a surface O. Thus,
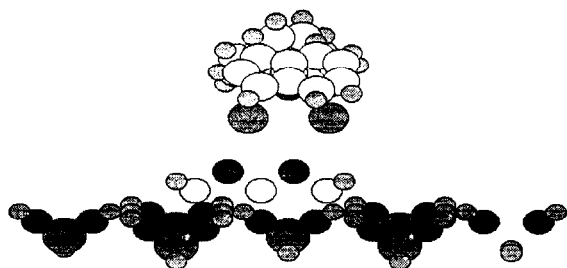
Zr comes down onto an O of a Si–O–Si group (see Fig. 16).

The adsorption, that is possible at both surfaces, is specially favored in the (111) AIS plane, where O and Si atoms are at the same level. The energy difference between both minima is 6 eV. Considering the (100) GEM plane, the species are possible but not they are not as stable as the species adsorbed on the (111) AIS plane (see Fig. 17). If both surfaces were available for adsorption, the zirconocene would probably adsorb onto the (111) AIS plane.

3.2.2. With AlO

The zirconocene is placed as the previous situation but the z coordinate is obviously longer (see Fig. 18).

The Al–O–Al string destabilizes the adsorbed species at both planes. In the case of the (111) AIS plane the perturbation is not so great. When the (100) GEM plane is considered, the interaction of zirconocene with the AlO-modified surface is repulsive (see Fig. 17).
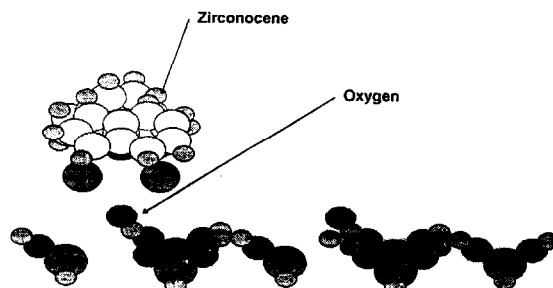

Fig. 14. EtInd$_2$ZrCl$_2$ adsorption on (100) GEM plane at 200°C/AlO.
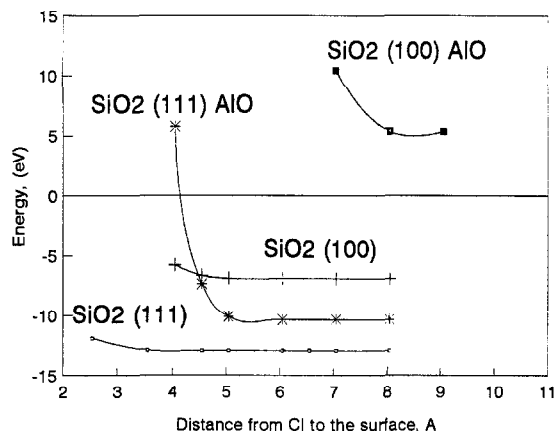

Fig. 16. EtInd$_2$ZrCl$_2$ adsoption on (100) GEM plane at 600°C.

Fig. 17. Adsorption energy versus $EtInd_2ZrCl_2$-surface distance (at 600°C).

The energy situation of the process on both planes and temperatures can be summarized as follows.

3.3. (100) GEM plane

When the pretreatment temperature is 200°C the minimum is near to -1.7 eV while it shifts to -7 eV when pretreatment is done at 600°C. Thus adsorption of $EtInd_2ZrCl_2$ seems to be more stable if the pretreatment temperature is 600°C.

When an AlO string is present the adsorption is drastically improved for SiO_2 modeled at 200°C (-10 eV). Interestingly an unfavorable situation is present with a 600°C pretreatment ($+5.2$ eV)
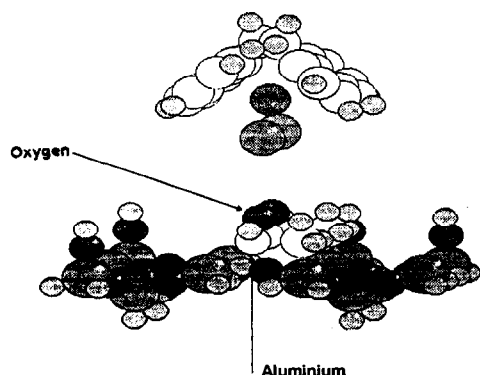

Fig. 18. (111) AIS plane at 600°C/AlO.

3.4. (111) AIS plane

At 200°C the minimum is near $+1$ eV while at 600°C the minimum shifts to -13 eV. The pretreatment at higher temperature makes possible a hindered form. When an AlO group is present, the adsorption is improved at 200°C (minimum at -7.0 e V) while at 600°C the minimum shifts to -10.5 eV.

4. Discussion

With metallocene catalysts, the usage of a support is a necessary step to achieve the desired activity and morphology, specially for gas phase industrial polymerization.

In the patent literature it is mentioned that the preferred way to prepare a very active metallocene supported complex is using a silica gel containing up to 40% water, which is contacted with an alkylaluminum compound to form an aluminoxane at the surface [12,13]. After that the support is treated with a metallocene solution, to prepare the precatalyst.

Another way to support the metallocene is treating the SiO_2 at high temperature (higher than 400°C but lower than 800°C) to dehydrate the surface. Following the thermal treatment the surface is contacted with the metallocene solution.

In this paper we aimed our effort to simulate two different situation of a SiO_2 support obtained via treatment at two different temperatures. The results show different trends.

When the SiO_2 is modeled at 200°C, without the AlO string the adsorption of $EtInd_2ZrCl_2$ is possible on the (100) GEM plane but not on (111) AIS. The Cl-H distance in this case is 3.106 Å. This implies that, without pretreatment with MAO, the adsorption of $EtInd_2ZrCl_2$ is only favored at (100) GEM plane of SiO_2, where the geminal OH are involved. The zirconocene is selectively adsorbed on the (100) GEM plane. When a string of AlO is added, the adsorption is strongly improved on both planes.

These results show that, dealing with amorphous SiO_2 treated at 200°C, the pretreatment with MAO increases the stability of $EtInd_2ZrCl_2$ adsorption. In this case, the chlorine and the Zr atom of the metallocene come down over an Al and an O of the AlO group respectively. The minimum of energy is located at an Al–Cl distance of 3.705 Å on the (111) AIS plane. Probably the amount of anchored zirconocene on the surface could be higher when the AlO group is present. The latter is in a good agreement with several results related to pretreatment of 'hydrated' silica with MAO and the subsequent improvement of zirconocene adsorption and activity of resulting catalysts.

If pretreatment is carried out at 600°C, the $EtInd_2ZrCl_2$ adsorption is favored without an Al–O–Al string on the surface. On the (100) GEM plane the adsorption is stable. The results show that the pretreatment at 600°C stabilize the zirconocene adsorption in this plane (-1.7 eV versus -7 eV at 600°C). When the (111) AIS is modeled at 600°C, the zirconocene adsorption is also possible preferring this plane to the other. On both planes the adsorption is possible but the Cl-surface distances are greater than 4 Å. When AlO is present the zirconocene is selectively adsorbed on the (111) AIS plane. This result implies that the treatment of silica at high temperatures, without a MAO pretreatment, increases the adsorption of $EtInd_2ZrCl_2$.

The main consequences of this EHMO calculation performed on the adsorption of a zirconocene on amorphous silica surface can be summarized as follows.

At 200°C SiO_2 surface is hydroxylated to a considerable extent. The zirconocene adsorption on the (111) AIS plane of SiO_2 does not produce a stable species. On SiO_2 (100) GEM plane it produces a stable and favorable zirconocene species adsorbed selectively. The AlO group makes stable the adsorption on both planes, specially on the (111) AIS plane. However, the most favorable form is located on the (100) GEM plane (-10 versus -7 eV). Experimental results are in agreement with our theoretical calculations. Chien et al. [2] report that SiO_2 heated at 350°C supports $EtInd_2ZrCl_2$ only if it is pretreated with MAO before the impregnation step with the zirconocene (up to 0.62% Zr). If silica is not pretreated with MAO it doesn't retain Zr. Soga [4–6] found that to support $Et(IndH_4)ZrCl_2$ (up to 0.75% Zr) it is necessary to pretreat SiO_2 at a moderate temperature (not more than 400°C) and subsequently with MAO. Our model at 200°C probably resembles the situation on surfaces obtained after treatment in the range 200 to 400°C.

At 600°C our results predict that the AlO group makes repulsive the interaction of the zirconocene with the surface, specially for the (100) GEM plane. The adsorption of $EtInd_2ZrCl_2$ on dehydrated surface (without AlO) generates stable species on both planes, specially on the (111) AIS plane (-13 versus -7 eV). Kaminsky and Renner [3] agree with these results: supporting $EtInd_2ZrCl_2$ through an impregnation step lasting 16 h at 70°C on a SiO_2 pretreated at 600°C, produces a solid with 1.46% Zr/g of SiO_2. If SiO_2 dehydrated at high temperatures is treated with MAO before the impregnation step, zirconocene is weakly bonded to the surface. Quijada et al. [24] report that SiO_2 treated at 500°C holds up to 5.4% Zr ($EtInd_2ZrCl_2$) after being in contact for 2 h at room temperature.

With these data concerning the reaction in binary or ternary systems, it can be concluded that between 400–500°C the SiO_2 suffer important structural changes related to dehydration that modify its behavior in zirconocene adsorption.

5. Conclusions

Our calculations predict that pretreatment with MAO can be useful in the case of a SiO_2 treated at low temperatures. If SiO_2 is dehydrated at high temperatures (more than 500°C) following the model of SiO_2 at 600°C here shown, the zirconocene is fixed in a more favor-

able way without MAO on the surface. The results are in agreement with recent publications.

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