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Car-Parrinello Molecular Dynamics Investigation of Active Surfaces and Ti Catalytic Sites in Ziegler-Natta Heterogeneous Catalysis

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SUMMARY: A first principles molecular dynamics study of various active surfaces and Ti catalytic sites is presented. We first review some of our recent results about $MgCl_2$ lateral cuts acting as a support for Ti catalytic sites and inspect the structure and stability of the standard binuclear model. We find that catalytic adducts $TiCl_4$ and Ti_2Cl_6, which are the standard precursors of the active catalytic system, can bind more or less efficiently to the support according to the morphology of the active surfaces. Furthermore, the activation and polymerization phases are shown to be critical in determining whether or not a particular site is stable and suitable to carry out the polymerization process. We also address the problem of regioselectivity. Finally, we have attempted for the first time a first principles study of the role of a typical donor phthalate elucidating its binding properties on the different substrate cuts and its behavior as a poisoning agent for the Corradini mononuclear active site. These studies are very preliminary.

Introduction

It is well known that Ziegler-Natta (ZN) catalysis is one of the most important industrial processes in the mass production of polyolefins with a high degree of stereoregularity[1,2)]. So far, unfortunately, very little is known about the intimate structure of the active centers and their role in the polymerization process. In fact, in heterogeneous systems the low percentage of active sites and the very fast reaction time scale pose severe limits to experimental probes. Recent developments in both theoretical algorithms and computer facilities now make it possible to simulate such a system with great realism, which, due to its complexity, could not be afforded in the

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past. Models and reaction pathways proposed since the very beginning of the discovery of ZN catalysis can be tested in detail and new virtual experiments can be done in order to provide a better insight. In a typical industrial $MgCl_2/TiCl_4$ system, the milling process of the substrate leads to the exposure of various surfaces. These are generally restricted to the lower Miller indexes, for which the energy cost is not excessive. On these $MgCl_2$ lateral cuts catalyst adducts can bind more or less strongly and with different symmetries3), so the control of these surfaces is a crucial issue in tuning the stereochemistry of the polymer. So far, Ti has been the most successful transition metal for heterogeneous ZN catalysis. Its efficient binding is assumed to be due to the similarity of the crystal structure (hexagonal) of Ti and Mg and to the very close ionic radii of Ti^{4+} (0.68 Å) and Mg^{2+} (0.65 Å), although no proof has yet been reported4).

Computational Details

We performed first principles simulations5) within the Becke-Lee-Yang-Parr6) gradient corrected density functional approach. The valence-core interaction was accounted for by norm-conserving Troullier-Martins pseudopotentials7). In the case of Ti and Mg non-linear core corrections were included8). Electronic wavefunctions were expanded in plane waves with an energy cut-off of 70 Ry for Ti. The $MgCl_2$ support consisted of a slab containing 32 formula units for the (100) surface in an orthorombic supercell of 17.673x14.560x28.000 $Å^3$ and 30 formula units for the (110) surface in a monoclinic supercell of 19.095x12.522x28.000 $Å^3$. In both cases the large z dimension ensures enough empty space to avoid spurious interaction with repeated images, since periodic boundary conditions were imposed. In each simulation the catalyst was placed on only one side of the slab, while the opposite side was kept fixed to the bulk crystal structure. The temperature (323 K) was controlled via Nosé-Hoover thermostat chain9) and the reaction paths sampled according to the Blue Moon ensemble theory10).

Results and Discussion

Active Surfaces

A detailed description of the active surfaces has been given elsewhere11,12). Here we recall briefly the main issues necessary to support the present discussion. Solid $MgCl_2$

has a layered structure in which each layer is saturated on both sides by Cl atoms. For this reason the prevalent surface is the basal plane (001). However this surface is inert and activation is achieved only after electron irradiation[13]. Since this is not the preparation adopted in industry, we did not pursue our investigations in this direction. Other cleavage planes can expose undercoordinated Mg atoms on which the catalyst can bind. Among these, one of the most discussed is the (100). The (100) surface as cleaved from bulk α-$MgCl_2$ leaves the central layer with 3-fold Mg atoms exposed (Figure 1 (a)). Since the component of the dipole moment orthogonal to the surface is non-zero, this surface is highly unstable. In fact it reconstructs (Figure 1 (b)) in such a way that at the end of the process all the exposed Mg are 5-fold coordinated. Other lateral cuts like (104) give rise to a support in which the exposed Mg are still 5-fold coordinated. However, in the case of (104), such a dramatic reconstruction does not occur, due to the fact that the surface is very flat and not affected by charge unbalance. Cleaving the support along the (110) (or (111)) direction gives another stable surface, on which the exposed Mg is 4-fold coordinated as described in Ref. 11. In this case the relaxation results only in a slight puckering of Mg atoms at the surface towards the bulk.

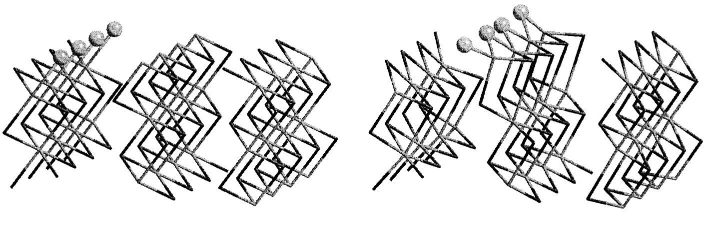


Fig. 1: Initial (100) $MgCl_2$ surface as cleaved from the bulk (a) and after the reconstruction process. Mg atoms are at the cross points of the sticks and indicated in light gray. The Cl atoms evidenced as balls jump from the left layer in (a) to the central layer in (b).

The general picture that emerges from these simulations is that active surfaces can expose only 2 kinds of Mg sites: either 5-fold or 4-fold. In the following, we shall consider the (100) and the (110) only as the lower Miller indexes representative of these two possibilities.

Active Sites

Mononuclear Ti Species and 2,1-Insertions

Mononuclear Ti sites on the (110) surface have already been discussed and we refer to our previous works for details[11,14)]. Here we address the question of the regioselectivity by investigating the 2,1-insertion in the alkylated 5-fold center, an issue that was left open in a previous paper[14)]. We recall that for this site, the stereoregular 1,2-insertion occurs with a barrierless complexation and that from the π-complex to the transition state leading to the isotactic insertion, a barrier of 45.19 kJ/mol has to be overcome, in agreement with experimental findings[15,16)]. The total energy gain, from the complex to the product, turned out to be 69.87 kJ/mol and the role of the substrate was analog to that of the bulky ligands in metallocene catalysis[17)].

If a 2,1-insertion is attempted on this same site, a stable π-complex cannot be located by simple geometry optimization or free dynamics. In fact, the reversed position of the large CH_3 group gives rise to strong steric interactions with the Cl atoms around the Ti center as can be seen from Figure 2.

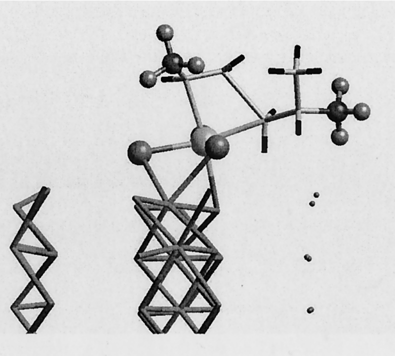


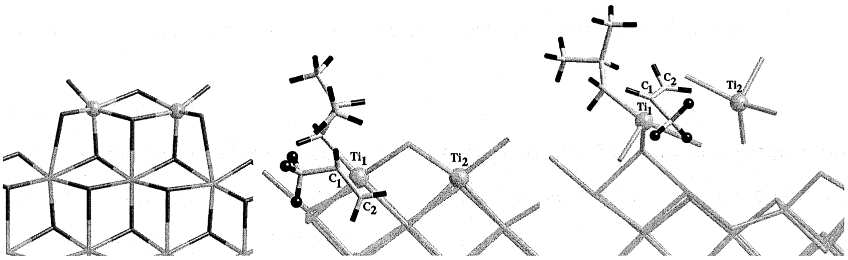
Fig. 2: TS of the regioirregular 2,1 Insertion. For the 2,1 π-state formation there is a free energy barrier of $\Delta F = 23.6$ kJ/mol. From this state there is an additional barrier of $\Delta F = 67.8$ kJ/mol with $T\Delta S = 48.1$kJ/mol

The complex was obtained only by a constrained dynamics approach, where the Ti-C distance between the Ti and the C_1 atom of the carbon double bond of the incoming propene was gradually reduced. The complexation energy barrier was found to be $\Delta E = 28.01$ kJ/mol, $\Delta F = 23.58$ kJ/mol for the free and total energy respectively. This is rather large, the entropic contribution being only TΔS=4.43 kJ/mol, and the complex is formed with a partial destabilization of the Ti center. In fact, the Ti adduct looses a bond with the substrate and weakens its binding to the support (see Figure. 2) The local geometry of this complex turned out to be almost the perfect geometry of a textbook example of a transition state. From this complex, we located a transition state at ΔF=67.78 kJ/mol and ΔE=115.90 kJ/mol, much higher than the insertion barrier relevant to the isotactic channel. In this case, the reaction coordinate was chosen to be the distance between the C_2 atom of the propene and the C_α of the growing polymer chain. The entropic contribution TΔS =48.12 kJ/mol is larger with respect to the complexation phase because of the great flexibility of the Ti-polymer chain-monomer group which is only weakly bound to the support and thus can rather freely oscillate and reorient. This result is in line with the conclusions drawn in [14)] and indicates that the stereoselective channel is favored also in comparison with the 2,1-insertion. Thus, as found in experiments, regioerrors are characterized by a very low probability.

Dinuclear Ti Species

As far as the (100) surface is concerned, any attempt to stick $TiCl_4$ adducts on the (100) surface turned out to be unsuccessful[12)]. This has very recently been confirmed experimentally by Prof. Freund's group[18)].

The (100) surface could instead accommodate binuclear Ti_2Cl_6 species, as proposed by the group of Prof. Corradini[3)]. Indeed, we found that such a configuration can form 5 bonds with the substrate (see Figure 3 (a)) and is characterized by a binding energy of 232.6 kJ/mol.



(a) (b) (c)

Fig. 3: The Ti binuclear center on (100) surface prior to alkylation (a), the complex as obtained by static calculations (b) and the destabilized complex after dynamics (c). (b) and (c) are top views of the same active site in (a). The gray balls indicate the Ti atoms, H atoms are shown in black with balls on the propene methyl group.

This site has the drawback that a large bond stress is present, due to the lattice mismatch between Ti and Mg. This is quite evident in the rather long side bonds (Cl-Mg=3.065 Å in Figure 3 (a)) in the adduct. As a result, after activation of the site by replacing one of the dangling Cl with a butyl group (Figure 3 (b)), a π-complex with propene in a *si* configuration could be formed after static geometry relaxation. However, if dynamics is allowed for a time of about 1.0 ps, a destabilization of the site occurs, resulting in the disproportionation 2Ti(III) $\rightarrow$ Ti(IV)+Ti(II). The whole process is energetically downhill and leads to an energy gain of 233.5 kJ/mol. We notice that this value is close to the binding energy of the Ti adduct before activation, thus accounting for the destabilization. The Ti site indicated as Ti_2 in Figure 3 is released as a free $TiCl_4$ molecule, while the remaining weakly bound Ti_1, carrying the complex, has a formal oxidation state II, being effectively bound only to the C_α carbon of the polymer chain ($Ti\text{-}C_\alpha$=2.273 Å) and to one of the two dangling Cl ($Ti\text{-}Cl_{dang}$= 2.291 Å). On these grounds, we can infer that binuclear Ti centers of this kind are not effective catalysts. It may be speculated that a more efficient binding of these configurations can be achieved if other Ti atoms are present as *trapped* atoms below Ti_1 and Ti_2, replacing part of the underlying Mg of the support. This can smooth the lattice mismatch and allow for better stability. This idea is close to the suggestion of Prof. Terano about the possible formation of *islands* of Ti$^{19)}$.

We also investigated the stability of a Ti_2Cl_6 dimer on the (110) surface. Under the attack of the incoming propene the dimer also destabilizes. Formation of a π-complex leads to a destabilization with ΔE_{gain}= 289.5 kJ/mol The Ti_1 carrying the polymer chain nearly looses contact to the surface and ends up formally in the oxidation state (II). It is interesting to see that in this fragment, the 2,1 orientation seems to be as possible as the 1,2 orientation This again puts emphasis that it is the surface that acts as a ligand to enforce the strict regioselectivity.

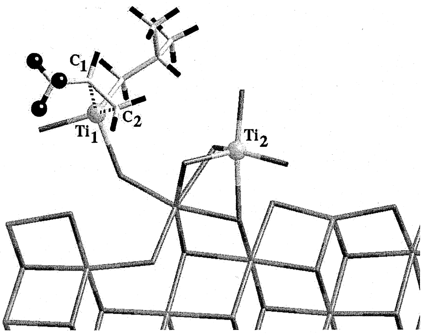


Fig. 4: The Ti binuclear center on (110) after π-complex formation. The dimeric structure has been destroyed. Instead, the 5-fold coordinate mono-Ti- species has formed. The system has undergone a disproportionation reaction with a Ti(IV) (5-fold species) and a Ti(II) carrying the polymer chain and the still π-coordinated monomer. The Ti(II) species is only weakly bound.

The main difference compared to the (100) dimer however is the spontaneous formation of the stable 5-fold mononuclear center already studied. We thus may consider the (110) dimer as a precursor of the stable five-fold site.

The Donor *di-n*-Butylphthalate

As a first attempt to address the role of a donor in a $MgCl_2/TiCl_4$, catalytic system, we considered the prototype molecule reported in Figure 5.

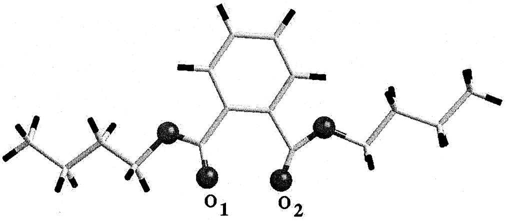


Fig. 5: Molecular structure of the common internal donor di-n-butylphthalate. Important for the effectiveness is the O_1-O_2 bond distance which has to be fit for the Mg-Mg distances found in $MgCl_2$

These kinds of phthalates of which the di-n-butylphthalate is a quite common species are known to improve the degree of stereoselectivity[20)] and are generally designed in order to fulfill the following requisites:

i) ability of coordinating on the MgC_2 support also in presence of Ti adducts,

ii) absence of secondary reactions with Ti during the catalyst preparation,

iii) absence of secondary reactions with both the metal-carbon bond and the growing polymer chain during the polymerization process.

The request i) is generally achieved by tuning the O_1-O_2 distance of the molecule in the range 2.7-3.8 Å while the other two aspects depend on the particular molecular structure and are the object of intensive researches in the molecular design domain[20)].

For the considered phthalate, the O-O distance can vary very easily in the range 3.37 and 3.76 Å, because the two hydrocarbon branches carrying the O atoms can reorient freely during a simple dynamics. The Mg-Mg distance of the exposed Mg on the relaxed active surface is equal to 3.67 Å and 6.36 Å for the (100) and (110) cuts respectively. It is then clear that such a donor can bind very efficiently on (100), while a less strong binding can be expected on (110).In fact, calculations for the (100) surface gave a binding energy of 91.63 kJ/mol with bond distances O_1-Mg_1=2.15 Å and O_2-Mg_2=2.25 Å for the relaxed structure reported in Figure 6(a).

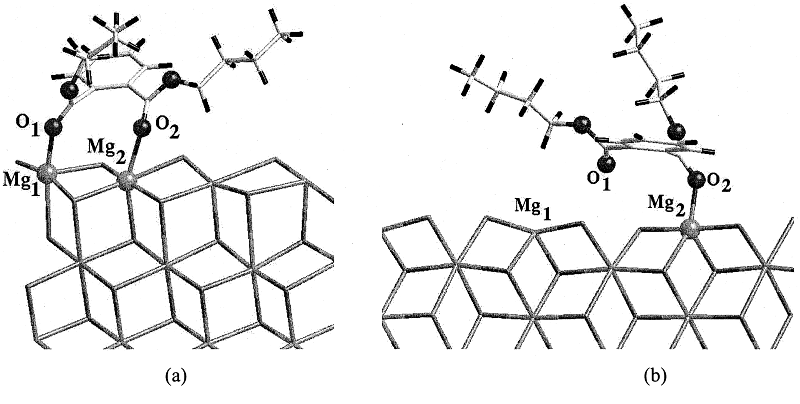


Fig. 6: Binding of n-butylphthalate on (100) (a) and (110) (b) surfaces of $MgCl_2$ obtained by Car-Parrinello Molecular Dynamics simulations. On the (100) surface, both oxygen atoms O_1 and O_2 can bind yielding a strong bond, whereas due to the mismatch on (110) only one Mg-O bond can be formed. Initial configurations with the ester oxygen next to Mg_1 attached to Mg_1 proved to be unstable and ended up in configuration (b) with only one strong bond.

Due to the larger Mg-Mg distance on (110), this same donor can form only one bond as shown in Figure 6(b). In this case the binding energy is 35.56 kJ/mol and the bond length O_2-Mg_1=2.085 Å. This bond almost restores the local geometry of Mg_1 to the bulk values, being now the Mg_1-Cl surface distances equal to 2.456 Å and the angle Cl-Mg-Cl = 177.0° very close to the 180° value typical of the bulk crystal.

The role of such a donor seems then to be that of a tuning agent able to control the surface morphology, in the sense that its strong binding on (100) - or, more generally, on surfaces exposing 5-fold Mg - prevents crystal growths presenting these surfaces and enhances or at least does not sensibly affect the (110) cuts. The lower binding of this molecule to (110), also in comparison with the binding energies of Ti adducts, makes in fact easy to displace this catalyst and replace it with Ti active centers.

On the other hand, we found that this same donor phthalate can bind on the activated mononuclear Corradini center with a binding energy of 84.10 kJ/mol, very similar to the binding of this same phthalate on the (100) bare surface. This is not surprising, since, in this case, the distance Ti-Mg where the donor binds (see Figure 7) is 3.781 Å, thus almost equal to the Mg-Mg distance of a typical (100) surface. The equilibrated phthalate-catalytic center bond distances are O-Mg = 2.203Å Ti-O =1.942 Å.

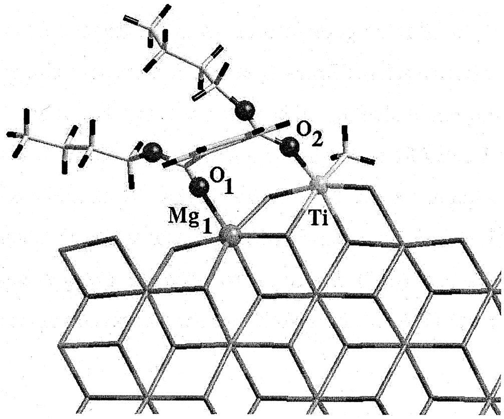


Fig. 7: Effective poisoning of the Corradini Center on (110) by the internal donor butylphthalate

This strong binding indicates that Corradini centers are easily poisoned by these donors and in their presence they cannot carry out the polymerization process. In the case of the 5-fold centers on this same surface, there are no possibilities to bind this phthalate so efficiently. As a consequence, 5-fold sites are not affected by its presence and can polymerize without being deactivated.

Conclusions

The interactions of Ti catalysts with a $MgCl_2$ support have been studied theoretically both prior to activation and during the polymerization process. Our study indicates that a strong binding of Ti is required in order to have a catalytic species able to carry out the polymerization. In fact, classical binuclear Ti models, which have been proposed as active sites on the basis of analogies with the violet $TiCl_3$ crystal structure, have been shown to destabilize under realistic reaction conditions. In agreement with experiment, 2,1 insertion has been found to be an unfavorable process with a high activation barrier. First attempts have been undertaken to investigate the role of an internal donor. We have shown that there is a selectivity in binding with the (100) surface as the preferable binding surface. From the results so far obtained, we found that the 110 surface is most important for the catalytic process. The active sites so far characterized are mononuclear sites. Further progress is necessary to understand the role of the donors and to find more candidates for active sites.

Acknowledgement

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