

Ziegler-Natta heterogeneous catalysis: a Car-Parrinello study

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Outline

- Main interests and computational details
- **MgCl₂** (100), (110) and (104) **active** surfaces
- **TiCl₄** and **Ti₂Cl₆** catalytic species
- **Active** centers and **complex** formation: *stability* problems under *real* reaction conditions
- α -Olefins polymerization: **ethylene** and **propylene**
- The role of a **donor phthalate** (few notes)
- Conclusions and perspectives (?)

Main interests

- ◆ **Ziegler-Natta** (ZN) catalysis is by far the most important industrial process in the production of polyolefins with high degree of **stereoselectivity**
- ◆ The reaction occurs at **room temperature** with a very **high reaction rate** and **low amount of catalyst**
- ◆ Experimental probes fail in recovering the microscopic picture due to the very fast reaction and the low percentage of active sites
- ◆ Quantum dynamical simulations can be a viable tool to study in an **unbiased way** and on **affordable time scale** active sites and the reaction pathway

Computational details

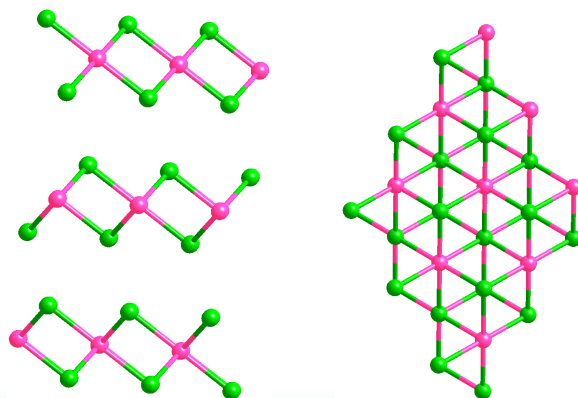
- ◆ **Car-Parrinello** molecular dynamics within **BLYP** density functional approach
- ◆ Valence-core interaction described by norm-conserving **Troullier-Martins** pseudopotentials with **non-linear core corrections** for Ti and Mg
- ◆ PW expansion of $\psi_i(\mathbf{x})$: $E_{\text{cut}} = 70 \text{ Ry}$
- ◆ Temperature control via **Nose-Hoover** thermostat chain
- ◆ Reaction path sampled within the **Blue Moon** ensemble theory

MgCl₂ simulation cells:

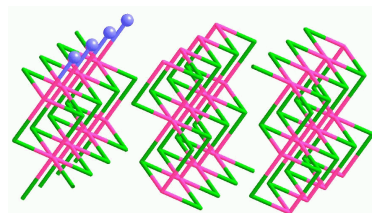
- ◆ Surface (100), orthorhombic, 32 formula units,
17.673 × 14.560 × 28.000 Å³
- ◆ Surface (110), monoclinic, 30 formula units,
19.095 × 12.522 × 28.000 Å³
 $a^b = 70.2^\circ$
- ◆ Surface (104), orthorhombic, 48 formula units,
14.560 × 21.711 × 28.000 Å³

MgCl₂ bulk crystal structure

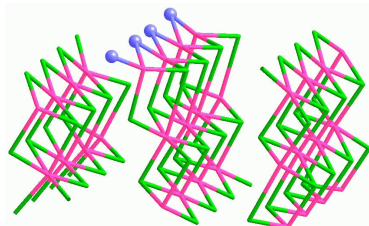
Space group: R $\bar{3}m$, a = 3.640 Å, b = 17.673 Å



MgCl₂ (100) surface

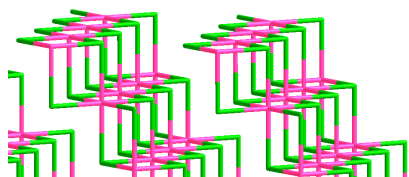


- ◆ Unrelaxed:
Mg-Cl = 2.526 Å
(exp. 2.530 Å)
ClMgCl = 180°

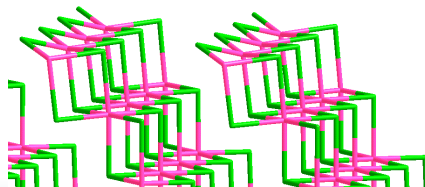


- ◆ Reconstructed:
Mg-Cl = 2.442 Å
 2.635 Å
 $\Delta E = 12.7$ kcal/mol Mg

MgCl₂ (104) surface

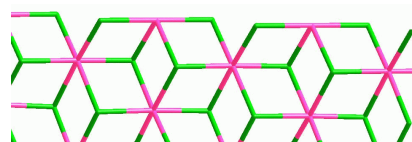


- ◆ Unrelaxed:
Mg-Cl = 2.526 Å
(exp. 2.530 Å)

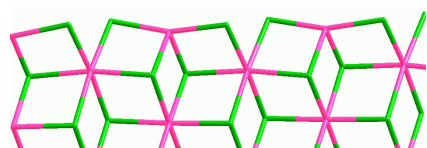


- ◆ Relaxed:
Mg-Cl = 2.421 Å
 2.597 Å
ClMgCl = 162.1°
 $\Delta E = 2.4$ kcal/mol Mg

MgCl₂ (110) surface

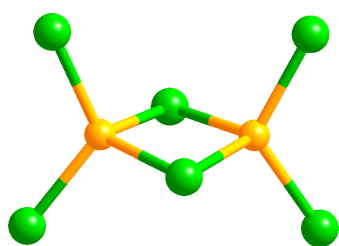


- ◆ Unrelaxed:
Mg-Cl = 2.526 Å
ClMgCl = 180°

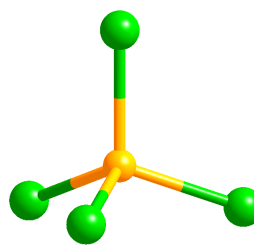


- ◆ Relaxed:
Mg-Cl = 2.322 Å
 2.403 Å
ClMgCl = 154°
ΔE = 3.4 kcal/mol Mg

Molecular geometries of the catalysts



Ti₂Cl₆
Ti-Cl^{bridge}=2.44 Å
TiClTi=93.7°



TiCl₄
Ti-Cl=2.24 Å
ClTiCl=109°

Deposition of the TiCl_4 catalyst

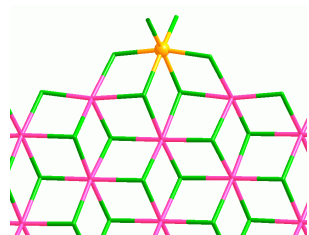
Ziegler–Natta Heterogeneous
Catalysis Reaction

Deposition of the catalyst on
the (110) surface of the support

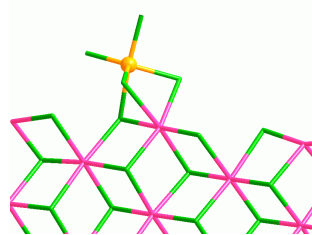
MPI

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Mononuclear Ti centers

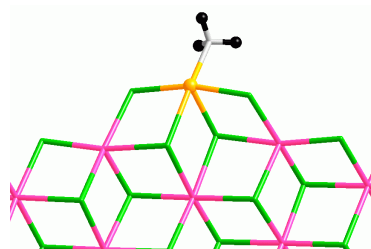


Octahedral Ti 6-fold on
 MgCl_2 (110) surface as
proposed by Corradini
and co-workers.
 $E_{\text{bind}} = 40.3 \text{ kcal/mol}$

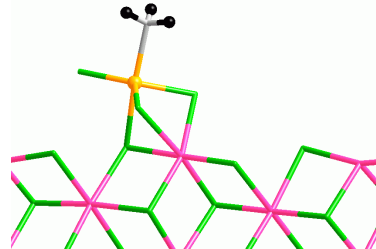


5-fold Ti site on MgCl_2
(110) surface obtained
from CPmd
 $E_{\text{bind}} = 29.4 \text{ kcal/mol}$
[*JACS* **120**, 2746 (1998)]

Active mononuclear centers



Active **Corradini** center:
removal of 1 dangling **Cl**
+ substitution of a **Cl** with
a **methyl** group.



Active **5-fold** center:
substitution of a **Cl** with
a **methyl** group.

Free energy calculation

- ◆ Select the reaction coordinate ξ to be monitored.
Our choice: $\xi = |C_1 - C_\alpha|$ (olefin-chain distance)
- ◆ Add to the Car-Parrinello lagrangean L^{CP} the constraint ξ : $L^{CP} \alpha L^{CP} + \lambda_\xi (\xi - \xi_0)$
- ◆ Compute the ensemble average $\langle \lambda_\xi \rangle$ according to the Blue Moon prescription
- ◆ Integrate the constraint force along the sampled path

$$\Delta F = \int_{\xi_{init}}^{\xi_{final}} \langle \lambda_\xi \rangle d\xi$$

First insertion of ethylene

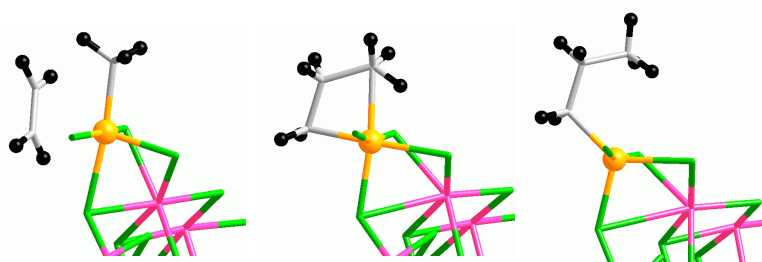
Ziegler–Natta Heterogeneous
Catalysis Reaction

First insertion of ethylene
in the Ti(IV) active site

MPI

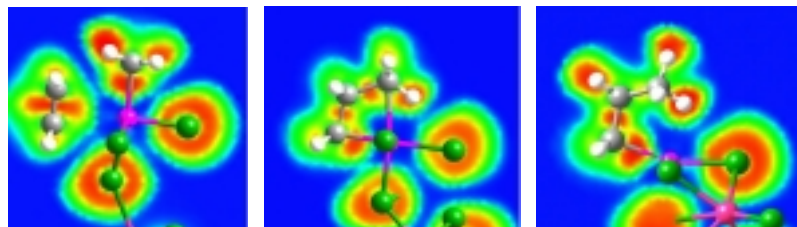
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Main phases of the insertion



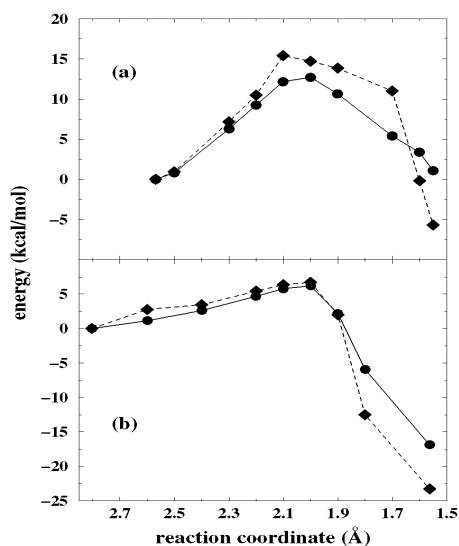
- The π -complex (left), the transition state (center) and the final product (right)
- Reaction coordinate: $\xi = |C_1 - C_\alpha|$
- The reaction is α -agostic assisted

Ethylene polymerization from mononuclear Ti



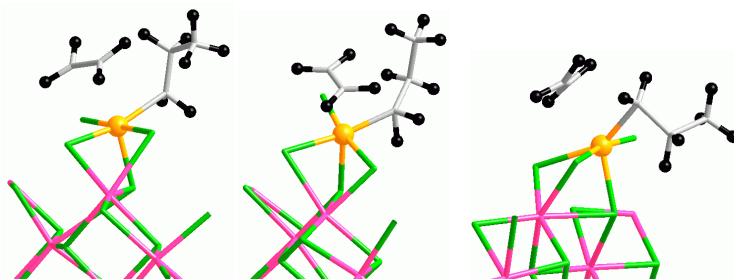
- ◆ ELF of the main steps of the ethylene insertion: the π -complex (right), the transition state (center) and the final product (right). ELF=0: **blue**, ELF=1: **red**
- ◆ ELF is projected on the plane containing the C₁ and C₂ carbon atoms (grey) of the ethylene and Ti (purple).

Energetics of the reaction:



- ◆ Free (solid line) and total (dashed line) energy profiles for the **Corradini** site (a) and for the **5-fold** site (b)

Reorientation of the alkyl chain



- ◆ As a response to the incoming of a new olefin, the chain displaces spontaneously along the substrate. The complex is dynamically stable.

Second insertion of ethylene

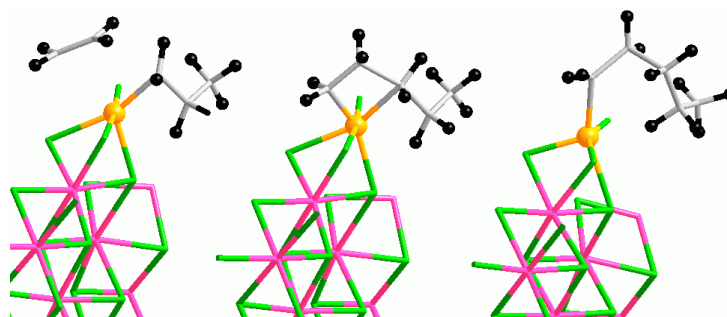
Ziegler–Natta Heterogeneous
Catalysis Reaction

Second insertion of ethylene

MPI

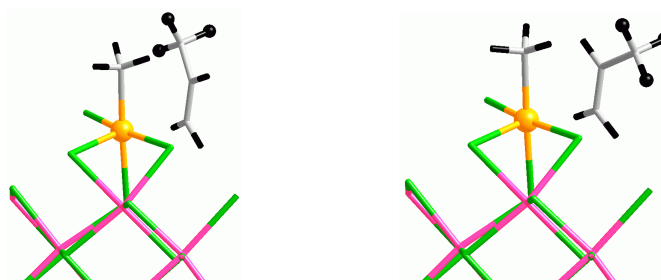
JRCAT

Second insertion of ethylene



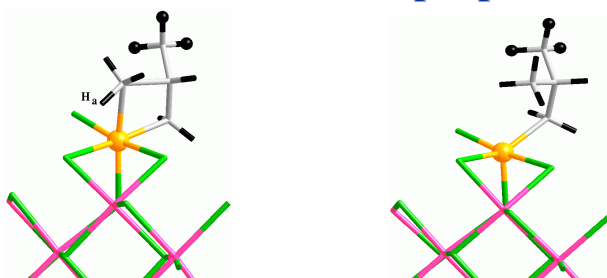
- π -complex (left), transition state (center) and final product (right) in a single snapshot
- Reaction is β -agostic assisted
JACS **120**, 2746 (1998), *Surf. Sci.* **438**, 1 (1999)

First insertion of propene



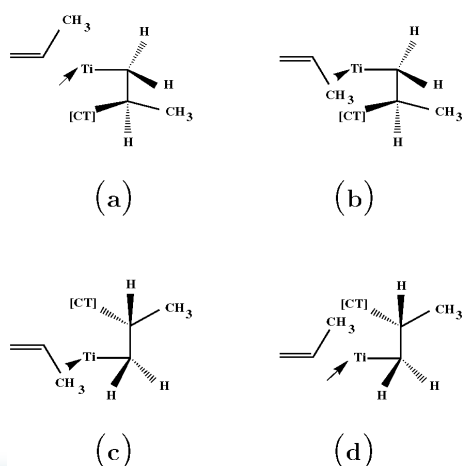
- ◆ The two possible π -complex enantiofaces for the first insertion of propene in the 5-fold active site
- ◆ The methyl group has to stay far from the support to avoid **steric repulsion**

First insertion of propene



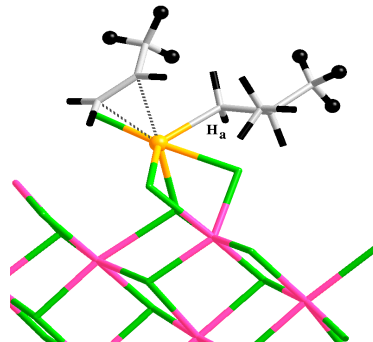
- ◆ Transition state (left) and final product (right) for one of the two enantiofaces. The other one would lead simply to the mirror image. Insertion is α -agostic (H_a) assisted.
- ◆ Energy barrier: $\Delta F=10.8$ kcal/mol (13.9 kcal/mol for the other enantioface).

Possible olefin orientations for propagation



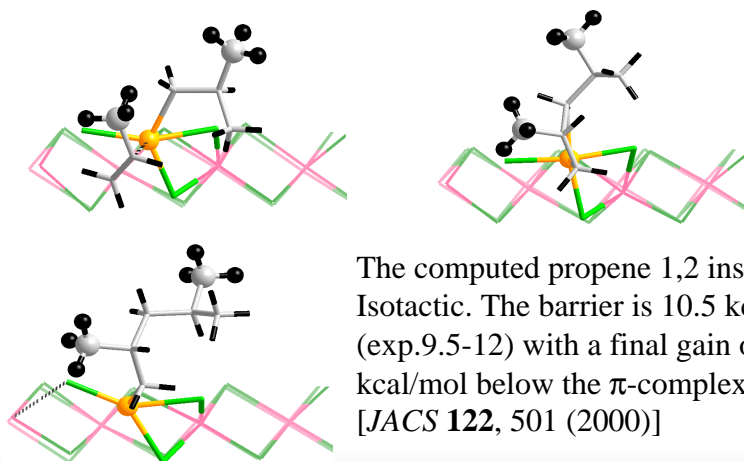
Only (a) can give a **barrierless** complex and a transition state lower by $\sim 7-8$ kcal/mol with respect to (b), (c) and (d).
The arrow indicates the position of the nearest Cl.

Complexation of a second propene



- ◆ π -complex of a propene oriented as in (a). The chain displaces along the substrate as in the case of ethylene.
- ◆ The insertion is α -agostic (H_α) also in the propagation

Propene polymerization from mononuclear Ti



The computed propene 1,2 insertion is Isotactic. The barrier is 10.5 kcal/mol (exp.9.5-12) with a final gain of 16.7 kcal/mol below the π -complex. [JACS 122, 501 (2000)]

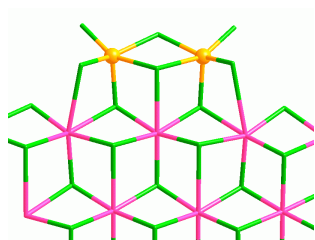
$C^{dangling}-Mg = 3.03-3.22 \text{ \AA}$

Complexation and insertion energies for ethylene and propene

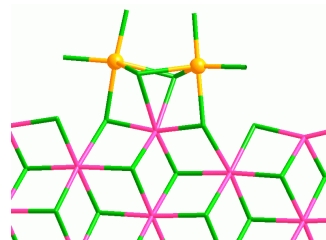
	π -complex (kcal/mol)	Insertion (kcal/mol)	Product (kcal/mol)
Ethylene	-8.4 ^a , -6.5 ^b	+12.7 ^a , +6.7 ^b	-5.8 ^a , -23.3 ^b
Propene (1,2)	-3.6 ^b	+10.5 ^b	-16.7 ^b
Propene (2,1)	+5.6 ^b	+16.2 ^b	(-1.0) ^b

a = Corradini site, **b** = 5-fold site

Binuclear Ti centers

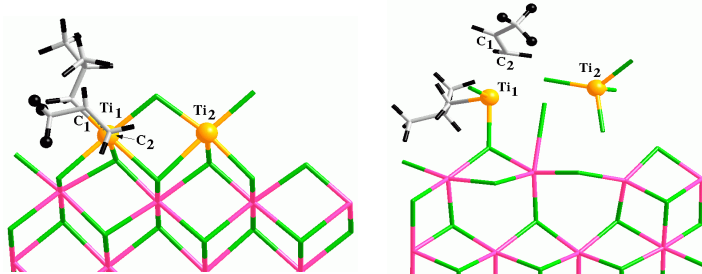


Corradini's Ti_2Cl_6 center
on MgCl_2 (100) surface:
 $\text{Mg}-\text{Cl}^{(\text{Ti})} = 2.673 \text{ \AA}$ (c)
 3.065 \AA (l)
 $\text{Ti}-\text{Cl}^{(\text{supp})} = 2.375 \text{ \AA}$
 $E_{\text{bind}} = 55.6 \text{ kcal/mol}$



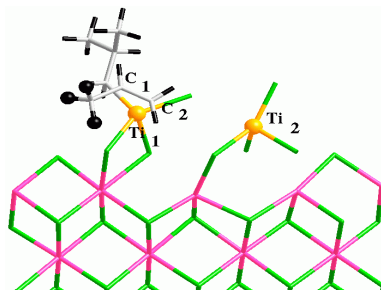
Ti_2Cl_6 center on MgCl_2
(110) surface from CPmd:
 $\text{Mg}-\text{Cl}^{(\text{Ti})} = 2.995 \text{ \AA}$
 $\text{Ti}-\text{Cl}^{(\text{supp})} = 2.469 \text{ \AA}$
 $E_{\text{bind}} = 33.6 \text{ kcal/mol}$

Propene polymerization from binuclear Ti



- ◆ **Singlet**: disproportionation $2\text{Ti(III)} \alpha \text{Ti}_1(\text{II}) + \text{Ti}_2(\text{IV})$ with a total energy gain of **55.8 kcal/mol**. The binuclear site is spontaneously **destabilized**.
- ◆ Final state: $\text{Ti}_1\text{-C}_\alpha = 2.273 \text{ \AA}$, $\text{Ti}_1\text{-C}_{\text{dangling}} = 2.291 \text{ \AA}$
 $\text{Ti}_1\text{-Cl}_{\text{support}} = 2.630 \text{ \AA}$

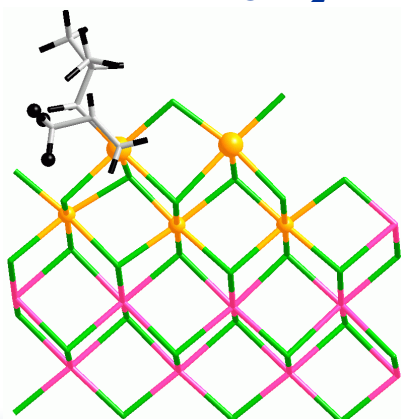
Destabilized binuclear Ti center (**triplet**)



- ◆ Dissociation $2\text{Ti(III)} \alpha \text{Ti}_1(\text{III}) + \text{Ti}_2(\text{III})$
- ◆ Final state **19.5 kcal/mol above the singlet**
- ◆ $\text{Ti}_1\text{-C}_1 = 3.033 \text{ \AA}$, $\text{Ti}_1\text{-C}_2 = 2.595 \text{ \AA}$

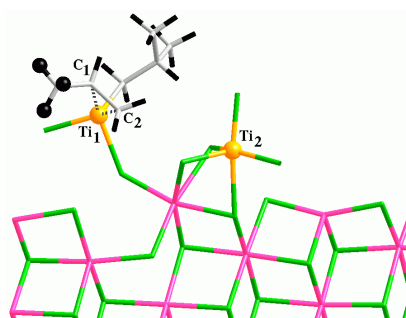
J. Phys. Chem. A **105**, 5096 (2001)

Possible stable binuclear Ti species on $\text{MgCl}_2(100)$ surface



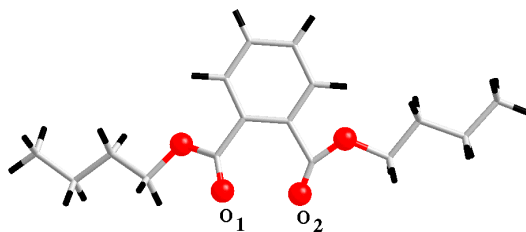
- ◆ Ti atoms (yellow) trapped **below** the active Ti_2Cl_6 on top (~Terano's islands)
- ◆ Gradual smoothing of the lattice mismatch between Ti (yellow) and Mg (pink)

Active binuclear center on (110)



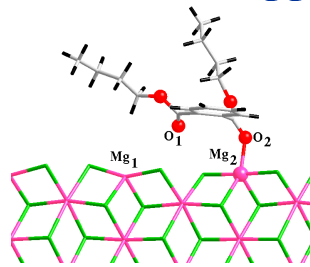
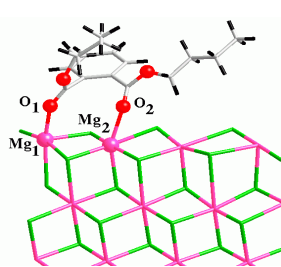
- ◆ Formation of π -complex leads to a destabilization with $\Delta E_{\text{gain}} = 69.2$ kcal/mol
- ◆ $\text{Ti}_1\text{-C}_1 = 2.185$ Å
 $\text{Ti}_1\text{-C}_2 = 2.161$ Å
- ◆ $\text{Ti}_1(\text{II})$ carrying weakly bound to the support
- ◆ $\text{Ti}_2(\text{IV})$: 5-fold site

Donor di-n-butyl phthalate



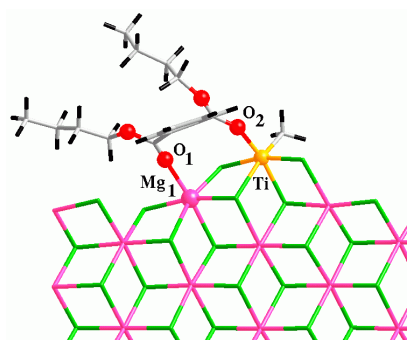
- ◆ Ability to coordinate to the support also in presence of Ti.
O₁-O₂ = 2.7-3.9 Å (**phthalates, diethers**)
- ◆ Absence of **secondary reactions** with the catalyst
- ◆ Absence of **secondary reactions** with the Metal-C bond and the growing polymer

Interaction of a donor with the support



	Mg ₁ -Mg ₂ (Å)	Mg ₁ -O ₁ (Å)	Mg ₂ -O ₂ (Å)	E _{bind} (kcal/mol)
(100)	3.674	2.150	2.246	21.9
(110)	6.360	> 4.0	2.085	8.5

Interaction of the donor with the active Corradini center



- ◆ $\text{Ti-Mg}_1 = 3.781 \text{ \AA}$, close to Mg-Mg distance on (100)
- ◆ $\text{Mg}_1\text{-O}_1 = 2.203 \text{ \AA}$
 $\text{Ti-O}_2 = 1.942 \text{ \AA}$
- ◆ Binding energy = 20.1 kcal/mol
- ◆ The center is **poisoned** by the donor
- ◆ No interaction with 5-fold

Conclusions (and perspectives)

- ◆ The role and the relative importance of various MgCl_2 **active surfaces** has been investigated
- ◆ Interaction of **Ti** species with the **support** has been studied
- ◆ The **polymerization** reaction has been investigated and the reaction pathway elucidated
- ◆ The problem of the **stability** of the active sites in a **realistic** system has been inspected
- ◆ The possible role of a **donor phthalate** has been addressed at a dynamical first principles level

Acknowledgements

- ◆ Hosrt Weiss, BASF AG, Ludwigshafen (Germany)
- ◆ Stephan Hueffer, BASF AG (Germany)
- ◆ Yoshitada Morikawa, JRCAT-AIST (Japan)
- ◆ Akinobu Shiga, Sumitomo Co. (Japan)
- ◆ Shinichiro Nakamura, Mitsubishi Co. (Japan)
- ◆ Minoru Terano, JAIST, Hokuriku (Japan)