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POLYOLEFIN HOMOGENEOUS CATALYSIS AT DFT LEVEL[*]

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The discovery of the homogeneous catalysts for the stereospecific and living behaviour has had important consequences to understand the Ziegler-Natta reaction. At DFT level, we give insight about syndiospecificity by means of an SN2-like mechanism and inhibition of termination reactions by Ti···F···H interactions.

The discovery of the octahedral homogeneous catalysts[1] for the stereospecific and living behaviour has had important consequences to understand the Ziegler-Natta reaction mechanisms.

The syndiospecific polymerization of propene has been known since the Sixties by means of homogeneous vanadium-based catalysts[2]. In the Eighties, the molecular mechanism of fluxional chiral complexes has been proposed[3]. According to the chain-end control mechanism, the syndiospecificity is based on the fluxionality of the catalytic site, by means of the cleavage and restoring of a Ti-N bond, which gives the site configuration inversion, followed by monomeric insertion. We give insight about the syndiospecificity of bis(phenoxy-imine)Ti Fujita-Coates' catalysts (Fig. 1a).

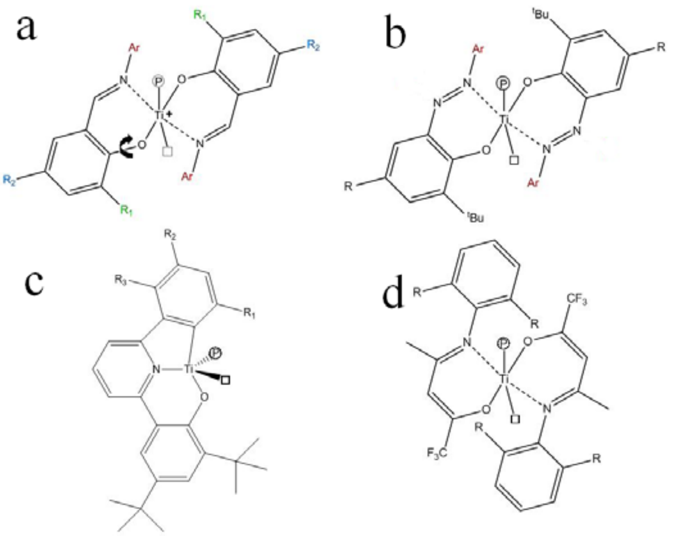

Fig. 1 - Molecular structures of active catalysts by Fujita-Coates (a), Hecht (b), Chan (c) and Mecking (d)

DFT calculations were performed and models were studied at the B3P86/TZVP level on the parallel platforms using GAUSSIAN09[4]. Normal mode analysis was performed and free energy corrections applied.

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Our calculations were performed with different catalyst models, studying the role of -F, $-C_6H_5$ and $-C_6F_5$ substituent groups, instead of a simple H, on iminic nitrogens.

The first target was the evaluation of the site fluxionality by means of the Ti-N *versus* Ti-O bond breaking. Calculations showed a lower energy barrier for Ti-N bond cleavage with a difference of about 20 kcal mol^{-1}, in accordance with literature models[1].

The second target was to study the role of the substituent group on the Ti-N bond breaking. Outcomes show similar values for the activation free energy at 29.8 kcal mol^{-1} for the -F, $-C_6H_5$ and $-C_6F_5$ models, in agreement with experimental findings, more stable than the -H one by about 12 kcal mol^{-1}.

Following, the activation step of the catalytic mechanism was studied. It should correspond to the inversion process of the complex chirality: in fact we observe a correlation between the Ti-N bond cleavage and the ligand *cis-trans* isomerisation by means of the -O-C- torsion angle (see Fig. 1a). Then, the open ring would invert the site chirality, reforming the bond with the opposite orientation.

The role of the propene coordination in the site chirality inversion has been taken into account. The -F model has been considered, and the relative stabilization, with respect to the monomer-free inversion, evaluated.

A free energy barrier of 21.7 kcal mol^{-1} for the activation-inversion process, lower of about 7 kcal mol^{-1} than in the calculations without olefin, has been calculated.

We define the observed mechanism as S_N2-like[5]: the entering monomer induces the *anti* N leaving, via a bipyramidal transition state, as shown in Fig. 2.

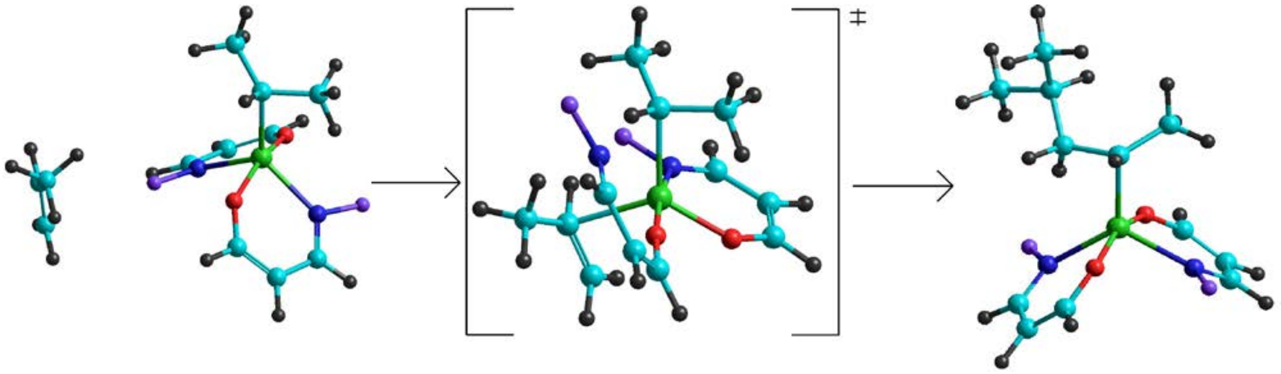

Fig. 2 - The S_N2-like mechanism for the inversion of the Fujita-Coates' catalyst

Recently, Hecht *et al.*[6] have developed a new class of octahedral bis(phenoxy-azo) complexes (Fig. 1b), able to give syndiotactic polystyrene. Likely, even this catalyst should require an inversion mechanism. Our DFT calculations on these catalysts are in progress.

Living polymerization is a hot topic in homogeneous catalysis: the synthesis of ultra-high molecular weight polyethylene and block copolymers is still challenging[7,8].

In the last years, the living polymerization has attracted a huge number of molecular modelling efforts. Nonetheless, the key role of fluorine non-bonded interactions remains controversial.

Fujita *et al.*[7] proposed the role of an $F\cdots H_\beta$ interaction between the fluorinated ligand and the growing chain, in order to explain the experimental living polymerization. Recently, Mecking *et al.* [8] reported that *ortho*-F substituted enolatoimines (Fig. 1d) also give living ethene polymerization, via F···Ti□interaction. This catalyst is currently under study.

Chan *et al.*[9] extended the presence of these fluorine interactions to arylpyridine tridentate complexes (Fig. 1c) to explain the higher activity of fluorinated catalysts. They hypothesized a three-centres $H_\beta\cdots F\cdots H_\beta$ interaction with the growing chain during the polymerization, which should suppress β-elimination reactions.

Starting, we considered the relative stability of the Chan's complex conformers, evaluating two interaction schemes: a *fork* H···F···H interaction, or a *double-couple* H···F one. A slightly different stability, in favour of the first scheme, has been found with a $\Delta E = 1.6$ kcal mol^{-1}.

The higher stability of the fork scheme could be due to the optimal orientation of the fluorine tetrahedral sp^3 AOs' towards the hydrogens.

In the second set of calculations, we highlighted the role of fluorine atoms and the stabilizing effect of H···F interactions.

The lowest energy conformer shows a Ti···F···H$_\beta$ fork interaction which closes a 5-membered ring, involving the two last carbons of the growing chain. In all calculated models, the agostic Ti···F bond is obtained. The H···F interaction is related to the rotation of the -CF$_3$ group, and gives a substantial contribution to the stability of the system: a conformational eclypsed-staggered equilibrium gives a transition energy barrier of 8 kcal mol^{-1} (Fig. 3). In this way, our findings[10] summarize the ideas of both Chan's 3-centres and Mecking's Ti-fluorine bonds, while the H$_\beta$···F···H$_\beta$ fork scheme doesn't seem to stabilize the complex during the polymerization.

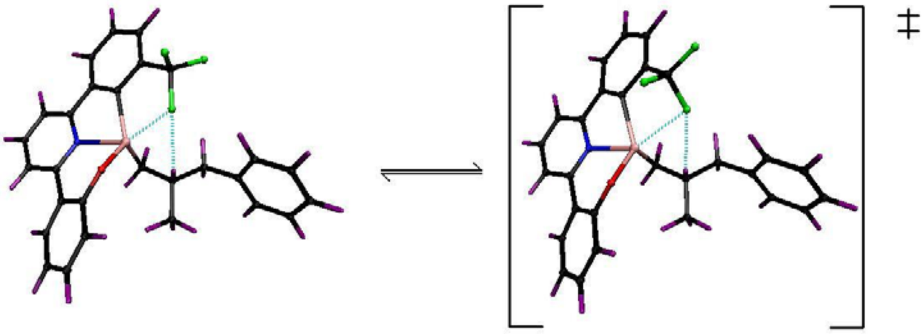

Fig. 3 - The conformational equilibrium for the most stable structure, for Chan's catalyst during the propagation step

The stability of the fork interaction can derive from the optimal overlap between the involved fluorine sp^3 lone pairs and a titanium empty 3d orbital.

In conclusion, the living polymerization originates from the bridged Ti···F···H$_\beta$ interaction, which inhibits the H$_\beta$ transfer to the metal or to the monomer in the termination reactions, increasing the relative transition state barriers.

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