An Empirical Correction Term to Density Functional Theory for the Description of the $TiCl_4$-Lewis Base Complexes

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Summary: Calorimetric and computational investigation on the interaction of $TiCl_4$ with some Lewis bases (esters and ethers) is presented. The bases were chosen for their relevance in heterogeneous Ziegler-Natta polymerization of propene. Comparison of the theoretical data with the calorimetric data indicates that calculations consistently underestimate the experimental binding energies. In light of this consistency, we propose that an empirical correction term added to the theoretical binding energies could represent an empirical solution for the prediction of the $TiCl_4$/donor binding energies with reasonable accuracy.

Keywords: density functional theory; heterogeneous catalysis; titration calorimetry; Ziegler-Natta polymerizations

Introduction

The catalytic system active in $MgCl_2$/$TiCl_4$-based Ziegler-Natta isospecific propene polymerization is the result of a delicate balance between several components, i.e. the $MgCl_2$ support, $TiCl_4$, the Lewis bases that can be added during or after catalyst preparation (usually referred to as internal and external donor, respectively), and the Al-alkyl species needed to activate the resulting pre-catalytic system.[1,2] This balance is the result of specific one-to-one interactions, such as the $MgCl_2$/$TiCl_4$, the $MgCl_2$/donor and the $TiCl_4$/donor interactions, although cooperative effects cannot be excluded. Thus, it is no surprise that many studies have been devoted to clarify the nature of these catalysts,[3–16] and of the mechanism of propene polymerization.[17–21] In this respect, computational chemistry has proved to be rather useful, since the experimental characterization of Ziegler-Natta catalytic systems surely presents formidable challenges.[22–27] However, one of the limitations of computational chemistry, when applied to Ziegler-Natta catalytic systems, is the lack of reliable experimental data to be used for the calibration of the computational data. This is quite a problem since, for example, accurate theoretical investigation of the competition between donors and $TiCl_4$ for adsorption on the $MgCl_2$ support strictly depends on the accurate prediction of the $MgCl_2$/$TiCl_4$ and $MgCl_2$/donor interactions, and surface coverage by adsorbed species also depends on the $TiCl_4$/donor interaction. Thus, any experimental and theoretical insight on these one-to-one interactions would contribute to shed light on these systems.

For these reasons, we recently performed a combined experimental and theoretical study of the structure and energetic of the interaction between $TiCl_4$

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and some Lewis bases representative of the most important classes of donors reported in the literature. Namely, alkoxysilanes, diethers, phthalates and succinates. Calorimetric experiments indicated that monofunctional and bifunctional donors result in $TiCl_4/L_2$ and $TiCl_4/L$ complexes, respectively, and that the enthalpies (ΔH°) of complexation is in the range of 80–120 kJ/mol. On the computational side, we discovered that Density Functional Theory (DFT)[28,29] calculations severely underestimated the experimental values, although there was quite good consistency in reproducing the relative experimental enthalpies of binding. At the same time, the computationally much more expensive approach based on the second order Møller-Plesset perturbation method (MP2)[30] predicted absolute binding energies in much better agreement with the experimental data, although consistency between ethers and esters was lacking.

Considering that the MP2 approach lacks of consistency, and that for the prohibitive computational cost (particularly if more extended systems which also include the $MgCl_2$ support should be investigated) cannot be the workhorse for this kind of calculations, it is clear that at the moment there is no computational tool that can be used for approximating the absolute binding energies of $TiCl_4$/complexes. In order to solve this issue, in this work we propose an empirical correction term that has to be added to the DFT calculated values in order to predict the absolute binding energies. Of course, it is clear that a rationalization of the weak performances remains an issue that deserves thorough investigations.

Computational Details

All calculations were performed with the TURBOMOLE 5.8 package.[31] The GGA functional of Perdew, Burke and Ernzerhof (PBE)[32,33] and the second order Møller-Plesset perturbation method,[30] were used. Geometry optimizations were performed at the DFT level only, and the MP2 energies were calculated using the DFT optimized geometries. A triple-ζ basis set augmented with two polarization shells on each atom and augmented with a s-function on C and O and a d-function on Ti, referred as def2-TZVPP in TURBOMOLE, was used.[34] To speed up the calculations the RI-J approximations were adopted.[35] The auxiliary basis set corresponding to def2-TZVPP was used. Solvation in 1,1,2,2-tetrachloroethane (TCE) was modeled using Klamt's COnductor-like Solvation MOdel (COSMO)[36] with a dielectric constant of 8.42 and a solvent radius of 2.79 Å. The cavity was defined using Klamt's optimized radii for H, C, O and Cl and a value of 2.223 for Ti. As TCE is a low polarity solvent, non-electrostatic cavitation, dispersion and repulsion terms are expected to play a non-negligible role. To evaluate these terms the Gaussian03 program[37] was run. Finally, all the binding energies were corrected of the Basis Set Superposition Error (BSSE) using Boys and Bernardi's counterpoise method.[38]

Results and Discussion

We first discuss the performances of DFT in reproducing correctly the geometries of $TiCl_4/L$ complexes. To this end, in Figure 1 we compare the X-ray structure of the $TiCl_4$/dimethyl-*o*-phthalate[39] with the DFT structure of the $TiCl_4$/diethyl-*o*-phthalate.

Visual inspection indicates that the DFT geometry reproduces the X-ray geometry with reasonable accuracy. The Ti–Cl bond distances are within 0.03 Å, while the Ti–O distances are within 0.11 Å, which can also be considered in reasonable agreement with the X-ray data. The Cl–Ti–Cl angle between the Ti–Cl bonds trans to the O atoms is only 3° wider in the DFT geometry, while the Cl–Ti–Cl angle between the trans Cl atoms is 7° smaller in the DFT geometry. In both structures the aromatic ring of the phthalate is similarly bent with respect to the plane defined by the Ti–O bonds. In conclusion, this analysis indicates that the

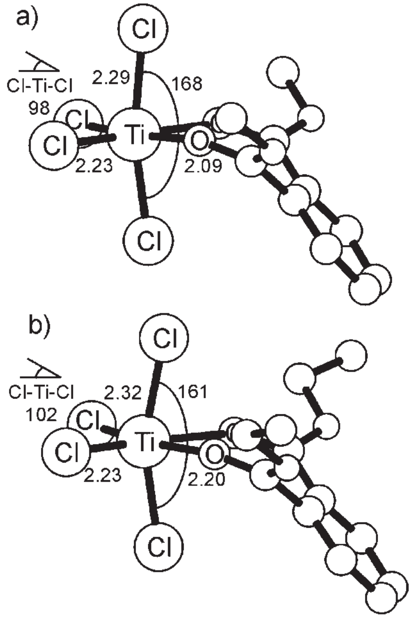


Figure 1.
Comparison between the X-ray structure of the $TiCl_4$/dimethyl-*o*-phthalate and of the DFT structure of the $TiCl_4$/diethyl-*o*-phthalate. Distances in Å, angles in deg.

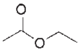
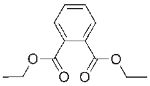
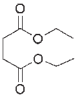
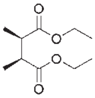
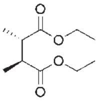
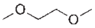
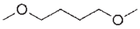
DFT approach we used reproduces the X-ray structure with reasonable accuracy.

The experimental enthalpies and the uncorrected DFT binding energies are listed in Table 1. As previously reported, the experimental enthalpies are severely underestimated by the DFT values. However, the data in Table 1 clearly indicate that the DFT values are consistently lower than the experimental values, and a simple statistical analysis results in a mean deviation of -43 ± 2 kJ/mol. The consistent discrepancy of the DFT binding energies from the experimental values is remarkable, considering that donors with definitely different steric and electronic properties, and even complexes with different stechiometries (i.e. $TiCl_4/L_2$ and $TiCl_4/L$ complexes) were considered. This suggests that adding an empirical correction term of 43 kJ/mol to the calculated DFT energies could be a very simple solution to obtain absolute binding energies with reasonable accuracy. Indeed, after the empirical correction of 43 kJ/mol is included, the empirically corrected DFT binding energies are in good agreement with the experimental data.

The consistent deviation of the DFT calculated binding energies from the experimental enthalpies, could suggest that the main source of error is in the deformation of the $TiCl_4$ moiety from the tetrahedral geometry of free $TiCl_4$ to the octahedral geometry in the $TiCl_4$/donor complexes. To investigate this point, we have analyzed the deformation of the $TiCl_4$ moiety from tetrahedral to octahedral, by fixing one Cl–Ti–Cl angle to 100°, which is close to the value of the Cl–Ti–Cl angle between the Ti–Cl bonds trans to the O atoms in the $TiCl_4$/donor complexes, while we opened the other Cl–Ti–Cl angle, which should represent the angle between the trans Cl atoms in the $TiCl_4$/donor complex, from 110° to 170°. The final geometry assumed, see Figure 2, is representative of the geometry of the $TiCl_4$ moiety in the $TiCl_4$/donor complexes. In particular, we compared the $TiCl_4$ DFT deformation energy with that calculated using the MP2 approach. In fact, our previous study indicated that the computationally expensive MP2 approach results in binding energies much closer to the experimental data, although it lacks of consistency between ethers and esters. This could suggest that the deformation energy calculated with the MP2 approach should be reliable.

The MP2 and the DFT curves reported in Figure 2 indicate that deformation of the$TiCl_4$ fragment from tetrahedral to octahedral requires a remarkable amount of energy, more than 100 kJ/mol. However, the difference between the approaches at high deformations, i.e. for Cl–Ti–Cl around 160°–170°, is slightly more than 10 kJ/mol, which suggests that the weakness of the DFT approach in calculating absolute binding probably is not in the energy required to deform $TiCl_4$ from tetrahedral to octahedral, but probably is in the Ti–O interaction.

Table 1.
Experimental enthalpy values and DFT binding energies, $-\Delta H_{exp}$ and $-(E_{DFT}$, respectively, from ref. [16], and DFT binding energies including the empirical correction term of 43 kJ/mol, $-\Delta E_{DFT+corr.}$, for formation of the $TiCl_4$-ligand complexes.

Ligand	Complex	$-(H^{\circ}_{exp}$ (kJ · mol^{-1})	$-\Delta E_{DFT}$ (kJ · mol^{-1})	$-\Delta E_{DFT+corr}$ (kJ · mol^{-1})
	ML_2	102	54	99
	ML	86	44	89
	ML	84	43	88
	ML	85[a]	45	90
	ML	90	47	92
	ML_2	120	78	122
	ML	103	61	106
	ML	90	43	88
	ML	88	45	90

[a] The experimental $-\Delta H^{\circ}_{exp}$ is for the 2,2′-i-Pr substituted donor.

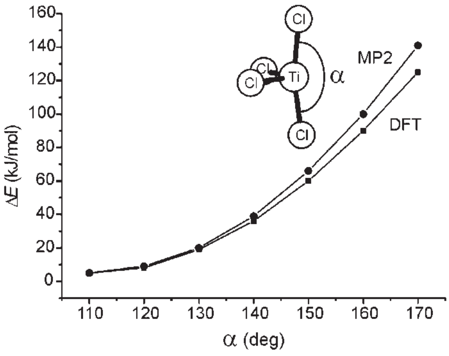


Figure 2.
DFT (■) and MP2 (●) energy curves relative to the deformation of the $TiCl_4$ fragment from tetrahedral to octahedral. The α angle should represent the angle between the trans Cl atoms in the $TiCl_4$/donor complex.

Conclusions

In this paper we have proposed an empirical correction term that could be added to the DFT $TiCl_4$/donor binding energies if absolute values are required. We remark that this correction is useless if relative binding energies are needed, i.e. different donors are compared. Of course, this correction term holds only for the specific DFT approach used here. It is clear that this approximation holds only for strictly related systems, i.e. differently substituted ethers and esters, and only for the specific computational approach used in this paper. However, considering that most of the donors used in heterogeneous Ziegler-Natta catalysis are indeed ethers or esters, the empirical correction term proposed here can have useful applications.

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