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Ziegler–Natta catalysts based on vanadium halides: a DFT study

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Abstract

Ziegler–Natta ethylene insertion into the carbon–metal bond for a number of fragments containing vanadium on different oxidation states as well as the halogen ligands has been studied by means of DFT. It is shown that the complexation and insertion energies are strongly influenced by the charge on the transition metal atom and, to some extent, by the electronegativity of the halogen atom. Complexation energy varies in the range −129 to −159 kJ/mol for charged species and −64 to −77 kJ/mol for neutral ones. Insertion energy follows a similar pattern and ranges from −28 to −62 and −82 to −100 kJ/mol, respectively. The calculated values are compared with the experimental results and different activities of catalysts based on VX_3 (where X denotes a halogen atom) are accounted for. Discussion of certain structural features of active sites, transition states and products is also given.

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1. Introduction

Despite the fact that homogeneous and heterogeneous catalysts of olefin polymerisation are of great commercial and industrial importance, relatively little is known about the influence of particular components of the catalysts on their performance. The vast majority of outstanding catalysts, for instance those developed by Kaminsky and Renner [1], Grubbs and coworkers [2], and Brookhart and coworkers [3], was developed as a result of experimental work. Therefore the search for new catalytic systems is based mainly on empirical rules. On the other hand, enormous progress in computational technology over the last decade made it possible to trace reaction paths and design precursors in order to adjust the catalytic properties before the expensive and time-consuming laboratory tests are performed. Certain general trends relating to the polymerisation process have become known before the end of the 20th century, with great contribution from, among others, Ziegler's [4–6] and Morokuma's groups [7]. The models considered by them converge to the real systems and the time between invention of a new catalyst and its characterisation by means of molecular modelling is becoming shorter and shorter [8].

The widely accepted mechanism of polymerisation developed by Cossee and Arlman [9,10], shown in Fig. 1, assumes that the catalytic active sites bind olefin molecules to form a π-complex (I). Then the π-complex undergoes insertion via a four-membered transition state (II) to form a product (III). The difference between the energy of (I) and substrates is called olefin uptake energy or energy of complexation, whereas insertion barrier is defined as the difference between energy of (II) and (I).

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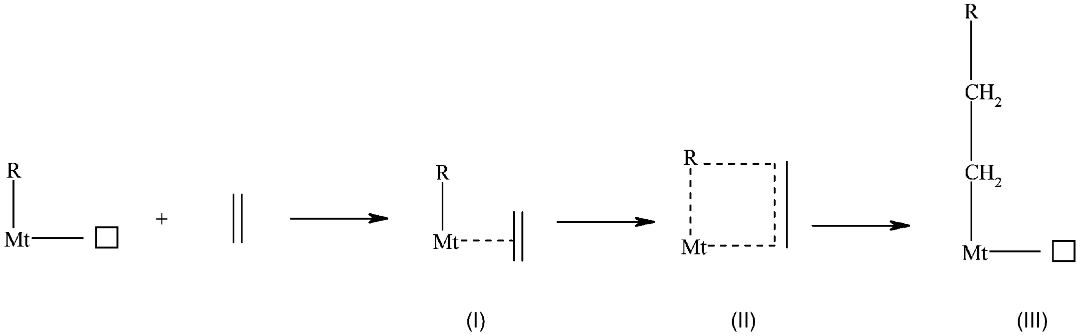

Fig. 1. Cossee–Arlman mechanism of polymerisation.

The magnitude of olefin uptake energy, insertion and termination barriers as well as insertion energy determines the overall activity of a particular catalyst. It is well known that the polymerisation process should be characterised by low insertion barrier and high termination barrier [4]. The process of insertion itself should be exothermic as well.

In this paper we have examined energetic profiles of ethylene polymerisation over a series of active sites derived from vanadium halides and discussed the variations in charge on the transition metal atom as a function of nature of the halogen atom. We also focus on the influence of a halogen atom as well as oxidation state of the transition metal on the catalytic activities of a particular system.

2. Computational details

Stationary points on the potential energy surface were calculated and characterised using the Gaussian 98 molecular modelling package [11]. The hybrid, three-parameter gradient-corrected density functional by Becke [12] Lee et al. [13] (B3LYP) and the LANL2DZ basis set [14–17], which includes the double-ζ basis set and effective core potential replacing chemically inert core electrons for V, Cl, Br, and I was applied. Pruned integration grids were used for all the elements except for iodine, where only a uniform grid was available.

Wavefunction stability was tested for representative structures and vibrational analysis has been carried out for each system considered. Charges were calculated using Mulliken population analysis [18] as well as Chirlian–Francl electrostatic potential fitting scheme CHelp [19].

3. Experimental

The appropriate precursor (1 mmol Mt) was ball-milled in a slurry with $[MgCl_2(THF)_2]$ (10 mmol) for 24 h. A sample (0.01 mmol Mt) was activated with an organoaluminium compound for 15 min at 323 K. Triethylaluminium, diethylaluminium chloride or tri-*iso*-butylaluminium were used as cocatalysts. The Mg:V molar ratio was 10:1 and the Al:V molar ratio was 500:1.

Ethylene polymerisation was carried out at 323 K in a stainless steel reactor (1 dm^3) equipped with a stirrer, in hexane at a pressure of 0.5 MPa. The polymerisation reaction was quenched with a 5% solution of HCl in methanol (150 ml). The polymer was filtered off, washed with methanol and dried at 303 K for 12 h at reduced pressure (5 hPa).

4. Results and discussion

In the following, we present the overview of DFT calculations and compare the results with the polymerisation tests carried out in our laboratory.

The activities of the heterogeneous catalysts obtained from vanadium(III) halides are given in Table 1. It is obvious that, independently of the cocatalyst applied, the most productive catalysts derive from VCl_3 and VBr_3. Their activities are greater by about one order of magnitude comparing with those based on VF_3

Table 1
Activity of catalysts based on vanadium(III) halides and different cocatalysts

Cocatalyst	Activity (kg PE/g V h)			
	VF_3	VCl_3	VBr_3	VI_3
$AlEt_2Cl$	6.85	83.80	63.24	3.42
$AlEt_3$	–	6.66	2.67	1.19
$Al(i–Bu)_3$	2.45	–	2.64	1.96
$AlEt_2Cl/AlEt_3$[a]	1.88	6.75	12.06	3.22
$AlEt_2Cl/Al(i–Bu)_3$[a]	4.21	–	9.39	3.24

[a] 1:1 mixture.

and VI_3. This phenomenon had to be explained by means of computer molecular modelling.

To achieve this objective we have selected a number of charged and neutral vanadium(III) and vanadium(II) fragments containing halogen atoms as well as an alkyl group and analysed energetic changes and charge evolution in the course of polymerisation. Similar fragments might be responsible for the activity of real systems, since the organoaluminium compounds added as cocatalysts play the role alkylating and reducing agents. In spite of the fact that real catalysts contain ethyl group, in our model methyl group is attached to the vanadium atom. Such an approach decreases the amount of time required to complete calculations. However, bearing in mind the importance of β-agostic interactions, which are absent in fragments containing methyl groups, we have also put some effort to study the $VCl_2C_2H_5$ fragment.

4.1. Energetics

Energetic profiles for the insertion of ethylene for the fragments mentioned above are given in Table 2. The first stage of the process, olefin uptake, must be sufficiently exothermic to compensate large negative entropy of complexation. According to Ziegler and coworkers [4], enthalpy of complexation must be lower than −40 kJ/mol. All the vanadium species studied by us fulfil this criterion. However, for the charged species, formation of a π-complex is about two times more exoenergetic comparing with the neutral ones. Insertion barrier is also markedly smaller, which makes us think that cationic active sites play a predominant role in the olefin polymerisation. Furthermore, in the case of many neutral fragments, insertion barrier is comparable with or even higher than the absolute value of complexation energy, thus making the process virtually impossible (see Fig. 2).

Closer analysis of energetic profiles for the charged $VXCH_3^+$ species reveals that for the fluorine-containing fragment, ethylene polymerisation is

Table 2
Energetic profiles for the insertion of ethylene for all fragments investigated[a]

Vanadium fragment	Complexation energy[b]	Insertion barrier	Insertion energy		Net energy of the process
			With respect to transition state	With respect to π-complex	
VF_2CH_3	−64	75	−100	−25	−89
VCl_2CH_3	−75	75	−93	−18	−93
$VCl_2C_2H_5$	−71	79	−98	−19	−90
VBr_2CH_3	−74	74	−94	−20	−94
VI_2CH_3	−72	74	−95	−21	−93
$VFCH_3^+$	−159	40	−28	+12	−147
$VClCH_3^+$	−155	39	−58	−18	−173
$VBrCH_3^+$	−143	39	−41	−2	−145
$VICH_3^+$	−132	40	−62	−22	−154
$VFCH_3$	−77	82	−83	−1	−78
$VClCH_3$	−75	70	−83	−14	−89
$VBrCH_3$	−74	68	−82	−15	−89
$VICH_3$	−73	66	−82	−17	−90
VCH_3^+	−129	60	−52	−8	−121
VCl^+	−653	–	–	–	–

[a] In units of kJ/mol.

[b] With respect to free ethylene and vanadium fragment.

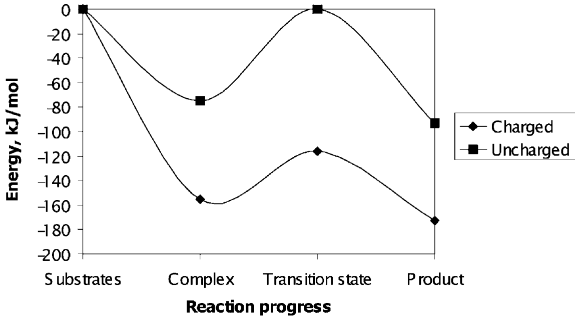

Fig. 2. Energetic profiles for the insertion of ethylene for charged ($VClCH_3^+$) and uncharged ($VClCH_3$) fragments.

endoenergetic with respect to the π-complex, which accounts for the fact that the catalyst obtained from VF_3 does not exhibit much activity in the process of ethylene polymerisation. Secondly, the nature of the halogen atom has a negligible effect on the insertion barrier and pronounced impact on the complexation energy. Therefore the latter influences the catalytic activity to a greater extent. In our series of $VXCH_3^+$ fragments, iodine-containing species bind ethylene least exoenergetically, which explains low activity of catalysts derived from VI_3, despite the negative insertion energy with respect to both the π-complex and isolated substrates.

In all the cases discussed, the magnitude of insertion barrier does not depend on the type of the halogen ligand. However, its lack in the VCH_3^+ fragment makes the complexation less exoenergetic. At the same time, insertion barrier remains high in comparison to other charged fragments, which may deteriorate performance of catalysts without any halogen ligands incorporated into them.

On the contrary, insertion into the C–Cl bond in the VCl^+ fragment is extremely exoenergetic (cf. Table 2). The resulting π-complex is therefore highly stabilised and non-reactive. The above explains the well-known fact that the olefin molecules do not undergo insertion into the C–Cl bond.

4.2. Charges

Charge variations during the insertion process are shown in Fig. 3. Cationic fragments, as may be expected, bear more positive charge. For all types of active sites considered, the charge on the vanadium atom depends on the halogen atom and decreases in the order: $F > Cl > Br > I$. This is consistent with the electronegativity trends and the V–X bond type, which gradually becomes more covalent. In almost all the cases studied, the process of ethylene complexation leads to the initial decrease of positive charge on the vanadium atom. As a result of insertion, the positive charge rises, but never reaches the initial value. Low catalytic activity of VI_3-derived catalysts may be attributed to the lowest charge on the transition metal atom in the catalytic centres containing iodine atom due to high polarisability of the I^- anion. It makes it difficult for the olefin molecule with its π-electrons to bind to the active site.

Similar tendencies hold true if the method employing electrostatic potential fitting is applied, although absolute values obviously cannot be compared. Fig. 4 shows charge evolution during insertion for the $VXCH_3^+$ species.

4.3. Structure

The presence of coordinatively unsaturated transition metal atom fragment leads to the formation of agostic interactions in the fragments investigated. According to Ziegler and coworkers [4], such interactions are much stronger in charged species comparing with neutral ones. To show an example we have optimised geometry of a neutral vanadium(II) fragment, $VClC_3H_7$, starting from the stationary point obtained for the cationic vanadium(III) species, $VClC_3H_7^+$. Both structures are shown in Fig. 5. There is a evidence of strong γ-agostic interactions in the charged fragment, since the $V–C_\alpha–C_\beta$ angle is merely 80.8° comparing with 101.7° for the neutral species.

Growing polymer chain is not coplanar with the V–X bond in the fragments studied due to agostic interactions as well. Energetic barrier related to the rotation of the chain is relatively low for neutral species (about 3 kJ/mol for the $VCl_2C_3H_7$), but remarkably high for the charged ones (21 kJ/mol for $VClC_3H_7^+$). Both transition states do not exhibit agostic interactions, thus rotation barriers provide another indication of strength of such interactions in charged and uncharged fragments.

The impact of agostic interactions on the polymerisation process is best seen if one compares the energetic profile for VCl_2CH_3 and $VCl_2C_2H_5$. There are

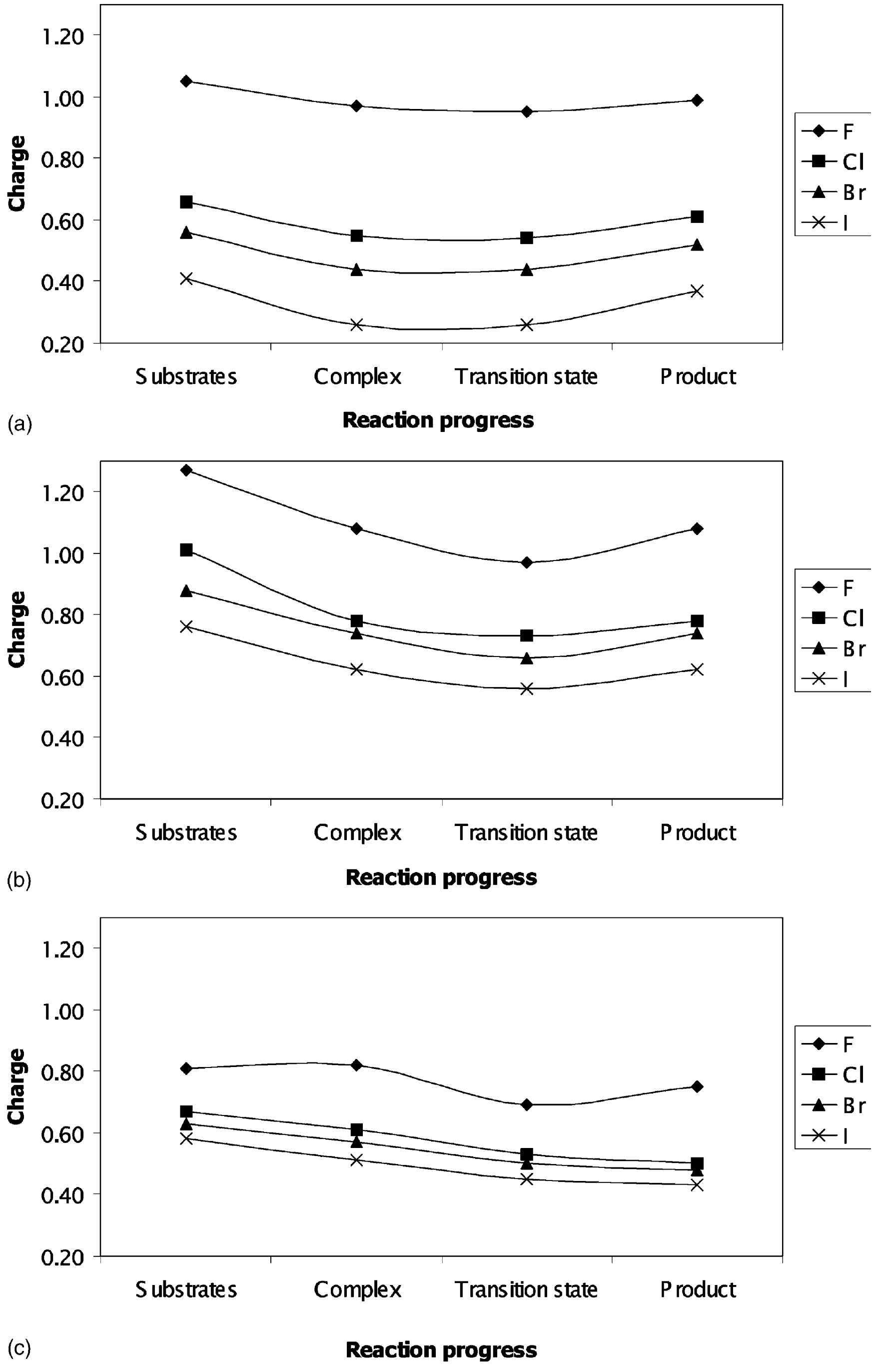

Fig. 3. Evolution of charge on the vanadium atom as a result of ethylene insertion for all fragments investigated: (a) neutral V(III) fragments; (b) charged V(III) fragments; (c) neutral V(II) fragments. Charges calculated using Mulliken method.

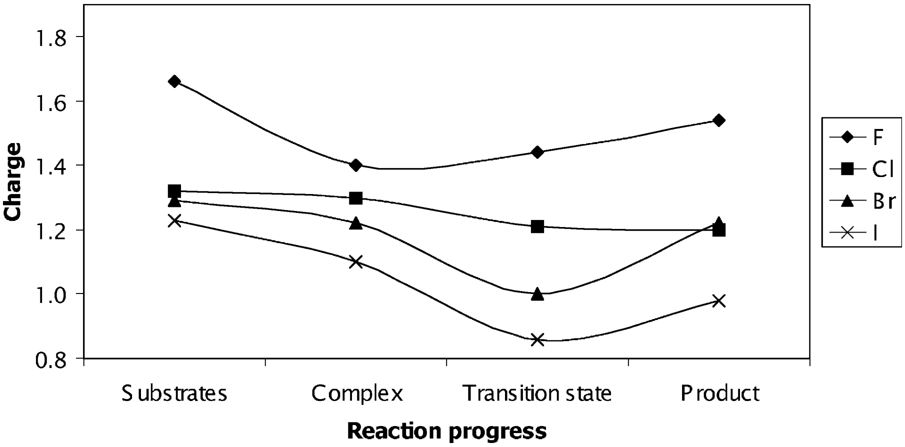

Fig. 4. Evolution of charge on the vanadium atom as a result of ethylene insertion for charged V(III) fragments. Charges calculated using Chirlian–Francl method.

some minor changes that include slightly less exoenergetic complexation, higher insertion barrier and more exoenergetic insertion. In general, agostic interactions do not influence the process dramatically.

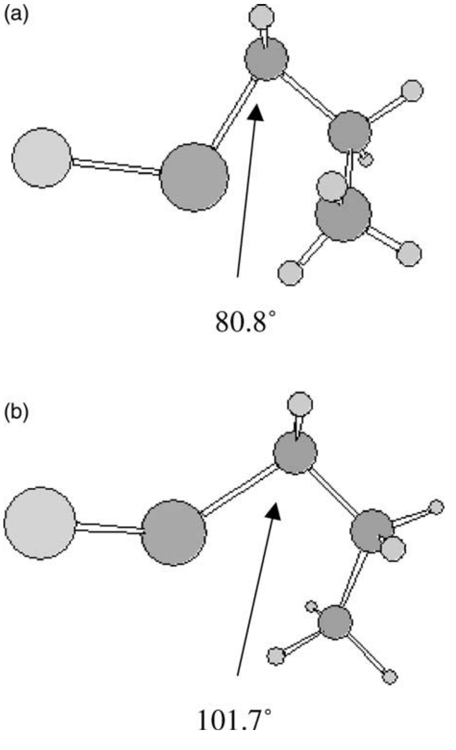

Fig. 5. Agostic interactions in: (a) $VClC_3H_7^+$ and (b) $VClC_3H_7$. Cationic fragment shows stronger γ-agostic interactions.

We have also found that in the case of $VXCH_3^+$ species, the X–V–C–H dihedral angle is equal approximately 60° for X $=$ F and Cl and exactly 0° for heavier halogens. Rotation barrier for $VClCH_3^+$ is relatively small (about 2 kJ/mol). The opposite is true for neutral vanadium(III) fragments, since only VF_2CH_3 and VCl_2CH_3 exhibit dihedral angle of 0°. Rotation barrier for VF_2CH_3 is also negligible (below 1 kJ/mol).

The potential energy surface for the π-complex of VCl_2CH_3 and ethylene is very flat with respect to the dihedral angle between the planes containing the V–C bond of the active site and C–C bond of ethylene. The rotation of C_2H_4 molecule is virtually barrierless (below 1 kJ/mol). However, all calculations carried out in this work were performed for the energetically most stable form, where the dihedral angle was 35.8°.

5. Conclusions

Comprehensive study of VX_3-derived fragments, which probably play a key role in the polymerisation of olefins, reveals certain rules that govern this process. Complexation is more exoenergetic and insertion barrier is lower for charged species. Neutral species show insertion barriers that are comparable with the complexation energy, thus preventing polymerisation. Nature of a halogen ligand determines the activity of a catalyst either by modification of energetic profile or influencing the charge on the transition metal atom. It has virtually no effect on the insertion barrier. Agostic interactions play important role in stabilisation of products that bear positive charge on the vanadium atom.

The laboratory polymerisation tests correspond to the results of theoretical calculations.

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