Prediction and Design of high potent *ansa*-Zirconocene Catalysts for Olefin Polymerizations: A Combined Quantum and QSPR approach

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Abstract: Homopolymerizations of ethene (ET), propene (PP), 1-butene (BT), 1-hexene (HX), and styrene (ST) by a *Rac* $[Zr\{1\text{-}Me_2Si(3\text{-}Pr\text{-}(\eta^5\text{-}C_9H_5))(3\text{-}H\text{-}(\eta^5\text{-}C_9H_5))\}ClCH_3^+]$ *ansa*-zirconocene catalyst were investigated using Density Functional Theoretical (DFT) calculations. The study unveils the following: (i) *ansa*-zirconocene is regio and stereoselective catalyst, (ii) (1,2)- is preferred over (2,1)-insertion and the (1,2)-*si* is the most favorable, (iii) Activity can be described by π-complex stabilization (ΔE_π) and intrinsic activation energy (E_a). Using E_a of ethene insertion step, QSPR models for activities of *ansa*-zirconocene were constructed. The best model predicts that potent catalysts should have small dipole moment and high positive charge on Zr.

Keywords: *ansa*-zirconocene, DFT, QSPR.

1. Introduction

The group 4 metallocenes, in particular *ansa*-zirconocenes are excellent catalysts for polymerization of ethene and higher α-olefins. Modification of the ligand structure provides an elegant way for rational tailoring of polymers with desired microstructure. Activities of metallocene catalysts depend on type of ligands (cyclopentadienyl (Cp), fluorenyl (Flu), or indenyl (Ind)) and numbers (one or two atoms) and types (C or Si) of bridging atom owing to electronic and steric effects. In this work, we theoretically investigated polymerization of ethylene (ET), propylene (PP), 1-butene (BT), 1-hexene (HX) and styrene (ST) monomers catalyzed by *rac* $[Zr\{1\text{-}Me_2Si(3\text{-}Pr\text{-}(h^5\text{-}C_9H_5))(3\text{-}H\text{-}(h^5\text{-}C_9H_5))\}Cl_2]$ *ansa*-zirconocene. Since this compound is proved to be the most active catalyst for *rac* monosubstituted metallocenes.[1] The mechanism of the olefin polymerization was proposed by Cossee and Arlman (Figure 1a).[2,3] The insertion of PP, BT, HX, and ST can be either primary (1,2) or secondary (2,1) and on *re* or *si* faces (Figure 1b). For PP, BT, HX, and ST the regio and stereoselectivity were studied. In addition, the QSPR model was constructed for the polymerization of ET and the guide for design of more potent zirconocene were given.

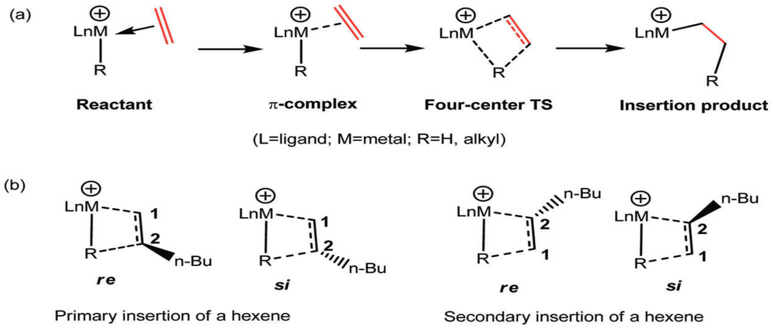

Figure 1. (a) Cossee−Arlman mechanism for alkene insertion into a metal−alkyl bond, **(b)** Four possible transition states for the insertion of a hexene into the M−R bond

2. Details of Calculations

The methylaluminoxane (MAO) co-catalyst was added to zirconocene catalyst to create the active site on the catalyst precursor. Hence, the cationic zirconocene active catalyst was created with one vacant site. Geometries as well as energy profiles for monomer insertions were calculated by the **B3LYP-D3** with cc-pVDZ basis set for C, H and Si and LANL2DZ pseudo potential basis set for Zr atom.

3. Results and discussion

Relative energy in kcal/mol of transition state structures for the four possible insertion modes, the primary (1,2)-*re* and (1,2)-*si*, the secondary (2,1)-*re* and (2,1)-*si* of PP, BT, HX, and ST monomers into a Zr-C bond with values of TS imaginary frequencies were given in Table 1. The results pointed to the primary (1,2)-*si* insertion as the most preferable insertion.

Table 1 Relative Gibbs energy (ΔG) in kcal/mol of TS for PP, BT, HX, and ST insertion to a Zr-C bond with values of TS imaginary frequencies (ν) in cm^{-1} and percent isotactic.

Insertion	**PP**		**BT**		**HX**		**ST**	
	ΔG	**ν**	**ΔG**	**ν**	**ΔG**	**ν**	**ΔG**	**ν**
(1,2)-*si*	000	-314.1	0.00	290.5	0.00	-293.3	0.00	-326.7
(1,2)-*re*	3.02	-322.9	3.07	-304.4	3.88	-306.5	3.18	-335.6
%isotactic*	97.64		97.81		99.33		98.13	
(2,1)-*si*	8.07	-331.2	8.30	-319.6	8.64	-323.1	5.55	-353.4
(2,1)-*re*	12.36	-346.0	12.44	-329.6	11.37	-335.2	12.95	-369.0

% isotactic = ((b-1)/(b+1))x100

b = exp($\Delta G/RT$) T = 70^0C or 343 K [45]

The effect of the monomer size on the polymerization activity was examined. Activities of polymerization can be explained by ΔE_π and E_a. The complex formed by ST insertion shows the strongest ΔE_π, while it also has the largest E_a. A good relationship between calculated activation energies (E_a) (Cat. 1-4, Table 3) and experimental activities (R^2=0.99) was found. Therefore, QSPR model of activation energies of *ansa*-zirconocene catalysts were sought**.** Seven additional catalysts (Cat.5 -11) were designed and computed for E_a. Ten molecular properties were used and the PLS technique was employed for fitting. Results were given in Table 2. The best QSPR model suggests that the potent zirconocene catalysts (with low E_a) should have low dipole moment and high positive charge on Zr atom.

Table 2 QSPR models on the intrinsic activation energy of 11 *ansa*-zirconocene catalysts (Cat. 1-11) with one and two descriptors shown with the square correlation coefficients (R^2) and square cross-validated (R^2_{CV}) values.

Model	**Equations**	**R^2**	**R^2_{CV}**
1	Ea = 2.6573* Dipole + 2.6703	0.70	0.63
2	Ea = -49.6400*Zr charge + 76.8231	0.65	0.58
3	Ea = 1.5459*Dipole - 28.8791* Zr charge + 45.0118	0.79	0.76
4	Ea = 1.4507*Dipole - 205.3139* LUMO - 37.2580	0.72	0.49

4. Conclusions

The primary (1,2) insertion with *si* face is the most preferable insertion path. They are around 3 kcal/mol lower than primary (1,2)-*re* and more 5 kcal/mol lower than secondary (2,1)-*si*. Thus, the *ansa*-zirconocene is regio and stereoselective catalyst for PP, BT, HX, PS polymerization. Intrinsic activation energy and π-complexation energy are important for predicting the catalytic activity. The intrinsic activation energy of the insertion step was found to be highly correlated with the experimental activity with R^2=0.99. Therefore, the intrinsic activation energies of 11 catalysts (Cat. 1-11) were used to constructed QSPR model. The result suggests that potent *ansa*-zirconocene catalysts should have less value of the dipole moment and more positive charge on Zr metal atom.

References

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