

## **Theoretical Prediction on Polyethylene Polymerization Activity on Phenoxy-imine Single-site Catalysts**

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### **ABSTRACT**

Eighteen Ti-phenoxy-imine (FI-Ti) based catalysts was theoretically investigated to clarify the relationship between the structural properties of catalysts and their polyethylene polymerization activity. Electronic properties of the FI-Ti catalysts were analyzed based on the density functional theory (DFT) with M06L/6-31G\*\* and LANL2DZ basis functions. The analysis results of QSAR equation with genetic algorithm showed that polyethylene catalytic activity mainly depended on the highest occupied molecular orbital (HOMO) energy level and total charge of the substituent group on phenylimine ring. The QSAR models showed good predictive ability ( $R^2$ ) and  $R^2$  cross validation ( $R^2_{cv}$ ) values greater than 0.927. Design concept is "Head-Hat" where the hat is phenoxy-imine substituents, and the head means the transition metals. So, for the new designed series, the phenoxyimine substituents still remained while the Ti metal was then replaced by Zr or Ni transition metals, namely FI-Zr and FI-Ni, respectively. Consequently, their polyethylene polymerization activities were predicted based on the obtained QSAR of FI-Ti models, and it is worth to note that the FI-Ni metallocenes catalysts trend to increase more polyethylene catalytic activity than that of FI-Zr complexes. Thus, the new designs of FI-Ni series are proposed as candidate catalysts for polyethylene polymerizations, with their predicted activities in the range of 35000-48000 kg(PE)/mol(Cat.)·MPa·h. Therefore, this combined DFT calculations and QSAR analysis are useful and straightforward methods for molecular design or catalysts' screening especially in the industrial researches.

### **1. INTRODUCTION**

Recently, the development of single site olefin polymerization is one of the hot issues in polyolefin industrials. Generally, to improve the polymerization catalytic performance, there are two desirable ways; modification of ligand or transition metal substitutions. [1-7]. Each fine-tuned ligand unit can offer various structural and electronic properties which influence the catalyst activity [3,8]. Particularly, phenoxy-imine can efficiently provide suitable bulky structure for ethylene polymerization process. The bidentate ligand was successfully studied by Fujita and co-workers through the generation of bis(phenoxy-imine) transition metal complex [9-15]. The formation of this organic bulky substituent enhances the catalytic activity thus initiates the polymerization. Therefore,

nowadays many researchers aim to develop efficient catalysts through ligand design and functionality modification [26-30]. In addition, the metal center was also investigated by substitution between early transition metals and late transition metals such as Ti and Ni, respectively [16,17].

The quantitative structure-activity relationship (QSAR) method, the approach to examine the activities of those catalysts in relation to their structures, is widely applied in catalyst researches [18-21]. Specially, this technique also enables better explanation of the different types of the electronic and steric factors which could affect not only bond length and bond angle but the highest occupied molecular orbital (HOMO) energy, lowest unoccupied molecular orbital (LUMO) energy and atomic charge as well. As a result, the conduction of this quantitative analysis can give an effective insight on the different catalysis efficiency based on their structure and electronic properties. Thus, in this work, the DFT optimization method and QSAR analysis were applied to investigate the electronic descriptors of FI-Ti metallocene catalysts related to their polyethylene polymerization activity. The genetic algorithm with multiple linear regression (GA-MLR) was selected to derive the QSAR equations. Based on the best obtained QSAR equation, it was then used to predict the polyethylene polymerization activity of the new design Zr- and Ni-phenoxyimine catalysts.

## 2. Experimental Data and Methods

### 2.1 Experimental Data

In this work, we studied the relationship between PE activity and basic electronic properties of FI-Ti catalysts. There were eighteen FI-Ti catalysts used as a training set for manipulating the QSAR equation. The structure details of each candidate and their experimental catalyst activity that were collected from Nikitin's work. For experimental data, the time-averaged activity of FI-Ti catalysts in ethylene polymerization is defined as

$$activity = \frac{M_{C_2H_4} \int_0^{\tau} W_p(t) dt}{C_{Ti} p_{C_2H_4} \tau}$$

where  $M_{(C_2H_4)}$  and  $p_{(C_2H_4)}$  denote the molecular weight and the pressure of ethylene, respectively;  $C_{Ti}$  - the initial concentration of a catalyst,  $\tau$  - polymerization time; and  $W_p(t)$  is the propagation rate given by

$$W_p = k_{eff} [Ti]_{act} [C_2H_4]$$

where  $k_{eff}$  is the effective rate constant (activity of a single active site), and  $[Ti]_{act}$  and  $[C_2H_4]$  denote concentrations of active sites and ethylene, respectively. For QSAR study, assumption of the same conditions for obtaining PE polymerization activity is required, thus, the catalytic activity should be determined by a composite function of  $k_{eff}$   $[Ti]_{act}$  which were reported by Nikitin et al. [22] (Table 1).

## 2.2 Structural Optimization Details

All the calculations were performed with the M06L density functional method using the Gaussian 09 software package [23]. The 6-31G\*\* basis set was used for C, O, N, H and Cl while, LANL2DZ was used for Ti, Zr and Ni. The structure of metal complexes was optimized and their energies were calculated to extract electronic and steric properties. Ten electronic properties collected: charges of metal center with Ti/Zr/Ni atoms, average charge of O, N and Cl, charges of substitution groups on phenoxy-imine ligands of **R1**, **R2** and **R3**, HOMO energy, LUMO energy, and bond distances of metal centers to surrounding O, N and Cl atoms

## 2.3 QSAR model

In QSAR studies, the choices of descriptors are the important steps to achieve the model with high correlation and prediction ability. Hence, genetic algorithm (GA) method as the effective technique to select the appropriate variables was used in this work. Catalytic activity was defined as the dependent variable, and there were totally 10 molecular electronic properties (descriptors) including atomistic charges and quantum-chemical descriptors which were fitted via the leave-one-out cross-validation coefficient value as fitness function. The genetic function approximation (GFA) algorithm implemented in the Materials Studio 7.0 package was used to construct the QSAR models[24].

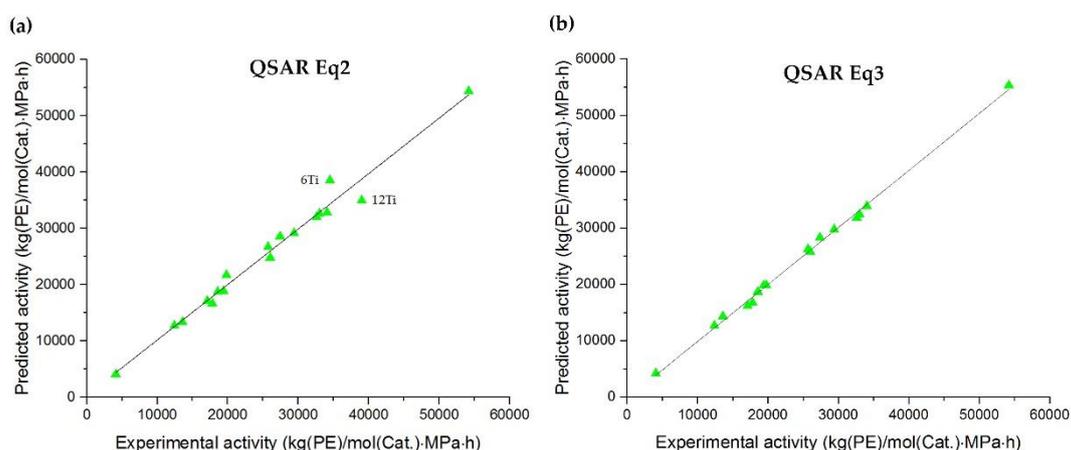
## 3. Results and Discussion

Based on the optimized FI-Ti structures, consideration on a symmetric skeleton structure of metallocene catalysts (see in inserted figure of Table 2). The obtained best QSAR models were listed in Table 3. As GA population of each parameter was considered to be the basic value of fitness for QSAR model, it found that the HOMO energy level exhibit the highest value followed by R3 total charge and then Ti charge with occurrences in population of 2097, 1067, and 351, respectively, whereas the rest of the descriptors only resulted in the range of 10-67 populations. This indicates that FI-Ti catalytic activity are closely related to HOMO energy level, R3 total charge and Ti charge which resulted in **Eq1** exhibiting a very good correlation with R-squared ( $R^2$ ) of 0.992. The obtained model also showed a high prediction ability with cross validated technique R-squared ( $R^2_{cv}$ ) of 0.936. In addition, the data distribution was evaluated by F-value, which resulted in 168.295. Although, it seems that this model is a good model, however, the population data of GA imposed a question on us that Ti charge population was actually very small compared with the other two descriptors. Furthermore, based on the "Head-Hat" designed concept, the Ti center would replace with another metals; thus, to avoid the direct effect of metal's partial charge, the elimination of Ti charge parameter was suitable to accomplish the better QSAR model.

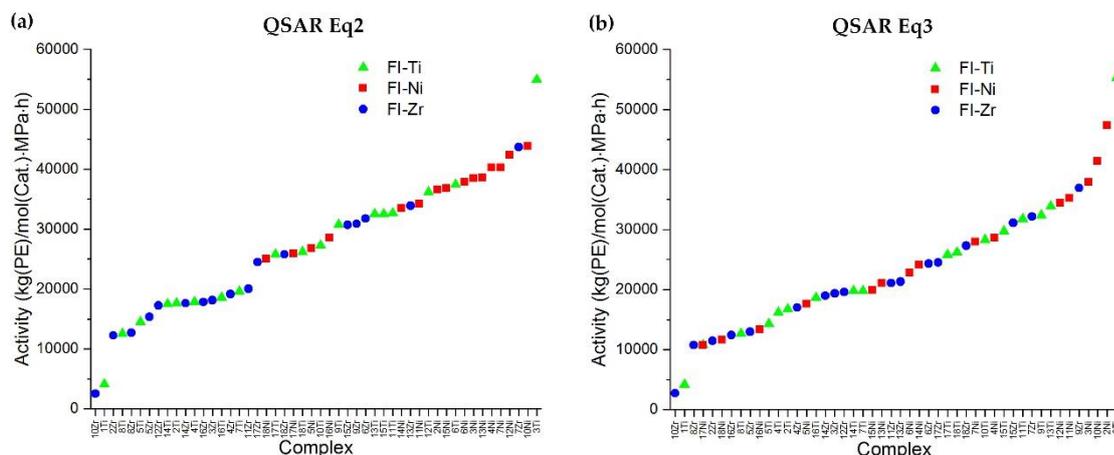
Generally, with exception of the predictive ability  $R^2$  and  $R^2_{cv}$ , the model with higher F-value is considered to be the better model. Although **Eq2** show very good correlation and predictable ability, if there were some choices for more

accurate predicted result, it would be done for improving the model. The graph shows that there are two outliers exhibiting more than  $|2|$  scaled residual value, which are complexes **6Ti** (2.128) and **12Ti** (-2.168). These outliers show high residual result on the predicted activity than the others and this reason lead to the error of whole model. So, to further improve the QSAR model, data of **6Ti** and **12Ti** complexes were eliminated, and then QSAR equation 3 (**Eq3**) was generated. The results indicated that the new model of **Eq3** achieved superior higher F-value of 564.305 which is twice of the previous one, while still exhibited high prediction ability with  $R^2$  of 0.997 and  $R_{cv}^2$  of 0.927. Therefore, both **Eq2** and **Eq3** were selected to predict the PE activity of FI-Ti catalysts using the GA-MLR of ramp function and their graphical plots between the experimental and predicted PE activities are depicted in Figure 1a and 1b, respectively.

We proposed the designed concept of “Head-Hat” where the hat is phenoxy-imine substituents, and the head means the transition metals. In this work, based on the training set of FI-Ti catalysts, the Ti metal center was then replaced by Zr or Ni transition metals while keeping the same phenoxy-imine substituents, namely FI-Zr and FI-Ni series, see in Figure 2. The new FI-Zr and FI-Ni complex structures were systemically built and were optimized using the same criteria of FI-Ti catalysts, and then their HOMO energy level and the **R3** total charge were extracted. The prediction of PE activities of new FI-Zr and FI-Ni catalysts were run via applying QSAR model **Eq2** and **Eq3**. Furthermore, to investigate the PE polymerization tendency performance, the results of the overall PE catalytic activities versus the Ti, Zr and Ni phenoxy-imine complexes were plotted by using the obtained **Eq2** and **Eq3** as depicted in Figure 2a and 2b, respectively. Based on the graphical plots, the trend of higher PE activity found in order of FI-Ni > FI-Ti > FI-Zr which agreed well on both QSAR **Eq2** and **Eq3** models



**Figure 1.** Plot of experimental PE activities versus predicted ones obtaining from **Eq2** (a) and **Eq3** (b) for FI-Ti catalysts

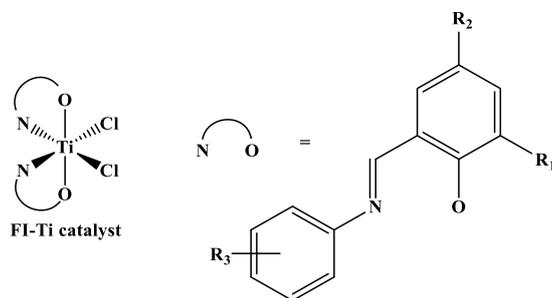


**Figure 2** Trend of predicted catalytic activity of all catalysts via **Eq2** (a) and **Eq3** (b).

#### 4. Conclusions

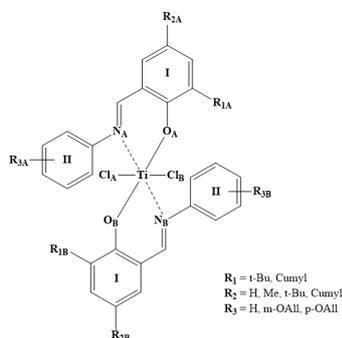
The phenoxy-imine catalysts were tailored by varying the substituent groups on the ligand units and also the metal center and their activities calculated via DFT calculation. After analyzing raw data of DFT simulation and experimental values of FI-Ti with QSAR method, the calculated properties from DFT approach illustrated the significant relation between realistic catalytic activity and the calculated electronic descriptors. The best obtained QSAR models, they consisted of two models of **Eq2** and **Eq3**, their  $R^2$  and  $R^2_{cv}$  value greater than 0.927. Insight the QSAR models, HOMO energy level and total charge of **R3** substituent electronic properties could be used to predict the PE activity of the FI-Ti catalysts. The design concept of “Head-Hat” was applied by replacing the head of Ti metal by Zr or Ni metals where the hats were still kept as phenoxy-imine substituents. Based on the obtained QSAR models derived from FI-Ti training set, the new metallocene catalysts of FI-Zr and FI-Ni series were then predicted their PE polymerization activities by using QSAR **Eq2** and **Eq3**. To purpose the candidate catalysts, the higher PE polymerization activities than 35000 kg(PE)/mol(Cat.)·MPa·h on those QSAR models was considered, and they found that based on all metallocene complexes which consisting of Ni as metal center atom showed better PE performance trend than that of Ti and Zr metal center phenoxy-imines results. Thus, the new purposed catalysts for PE polymerization are 2Ni, 3Ni, and 10Ni metallocene complexes. The present work shows that the combined DFT and QSAR studies are straightforward methods to derive the relationship between PE catalytic activity and electronic descriptors and the obtained QSAR model could be used for evaluating and designing new catalyst structures in search of promising polyethylene catalysts. This tailor-made study is more beneficial to industrial research and it is nicely uncomplicated method.

**Table 1** Chemical structure of FI-Ti catalysts with difference substituents (**R1**, **R2** and **R3**).



Complex	R1	R2	R3	Activity [A] (kg(PE)/mol(Cat.)·MPa·h)	ln[A]
1Ti	t-Bu	H	H	4100	3.613
2Ti	t-Bu	H	<i>m</i> -OAll	17800	4.250
3Ti	t-Bu	H	<i>p</i> -OAll	54200	4.734
4Ti	t-Bu	Me	H	17100	4.233
5Ti	t-Bu	Me	<i>m</i> -OAll	13600	4.134
6Ti	t-Bu	Me	<i>p</i> -OAll	39000	4.591
7Ti	t-Bu	t-Bu	H	19400	4.288
8Ti	t-Bu	t-Bu	<i>m</i> -OAll	12400	4.093
9Ti	t-Bu	t-Bu	<i>p</i> -OAll	33000	4.519
10Ti	Cumyl	H	H	27400	4.438
11Ti	Cumyl	H	<i>m</i> -OAll	32600	4.513
12Ti	Cumyl	H	<i>p</i> -OAll	34500	4.538
13Ti	Cumyl	Me	H	34050	4.532
14Ti	Cumyl	Me	<i>m</i> -OAll	19800	4.297
15Ti	Cumyl	Me	<i>p</i> -OAll	29400	4.468
16Ti	Cumyl	Cumyl	H	18550	4.268
17Ti	Cumyl	Cumyl	<i>m</i> -OAll	26000	4.415
18Ti	Cumyl	Cumyl	<i>p</i> -OAll	25700	4.410

**Table 2** FI-Ti Electronic descriptor data



Complex	Ti-charge <sup>a</sup>	O-charge <sup>b</sup>	N-charge <sup>b</sup>	Cl-charge <sup>b</sup>	R1-charge <sup>c</sup>	R2-charge <sup>c</sup>	R3-charge <sup>c</sup>	HOMO <sup>d</sup>	LUMO <sup>d</sup>	E-Gap <sup>d</sup>
1Ti	1.235	-0.704	-0.586	-0.374	-1.062	0.136	0.136	-0.199	-0.131	1.840
2Ti	1.232	-0.703	-0.585	-0.374	-1.062	0.345	-1.117	-0.197	-0.129	1.858
3Ti	1.247	-0.706	-0.588	-0.376	-1.057	0.130	-1.230	-0.194	-0.127	1.843
4Ti	1.234	-0.707	-0.589	-0.377	-1.058	-0.450	0.134	-0.193	-0.129	1.736
5Ti	1.227	-0.705	-0.589	-0.378	-1.062	-0.446	-1.109	-0.191	-0.126	1.770
6Ti	1.250	-0.709	-0.592	-0.380	-1.055	-0.442	-1.134	-0.191	-0.124	1.812
7Ti	1.252	-0.713	-0.610	-0.372	-1.056	-1.083	0.134	-0.197	-0.129	1.863
8Ti	1.235	-0.707	-0.588	-0.380	-1.033	-1.054	-1.097	-0.191	-0.124	1.817
9Ti	1.236	-0.707	-0.586	-0.381	-1.030	-1.054	-1.116	-0.187	-0.124	1.720
10Ti	1.243	-0.708	-0.607	-0.362	-1.147	0.139	0.136	-0.198	-0.133	1.765
11Ti	1.273	-0.706	-0.603	-0.372	-1.303	0.137	-1.129	-0.199	-0.130	1.867
12Ti	1.232	-0.694	-0.578	-0.374	-1.254	0.122	-1.131	-0.189	-0.124	1.765
13Ti	1.242	-0.696	-0.584	-0.376	-1.248	-0.026	0.133	-0.189	-0.125	1.739
14Ti	1.269	-0.707	-0.606	-0.376	-1.302	-0.445	-1.125	-0.191	-0.127	1.764
15Ti	1.224	-0.700	-0.579	-0.376	-1.257	-0.432	-1.121	-0.185	-0.123	1.688
16Ti	1.286	-0.703	-0.538	-0.385	-1.222	-1.353	0.120	-0.189	-0.121	1.856
17Ti	1.236	-0.705	-0.602	-0.370	-1.216	-1.350	-1.101	-0.189	-0.123	1.794
18Ti	1.270	-0.709	-0.598	-0.384	-1.262	-1.305	-1.102	-0.190	-0.125	1.750

a = partial charge (e), b = average charge (e), c = average of total charge of substituent group (e), d = in *Ha* unit

**Table 3** Statistical results of QSAR equations on FI-Ti series.

No	Equation	R <sup>2</sup>	R <sup>2</sup> <sub>cv</sub>	F-value
<b>Eq1</b>	$\ln(\text{Activity}) = 26.09 * \text{ramp}(\text{R3 Charge} + 0.22) - 7.47 * \text{ramp}(\text{R3 Charge} + 1.18) + 497.87 * \text{ramp}(\text{HOMO} + 0.19) - 494.72 * \text{ramp}(\text{HOMO} + 0.19) - 7.81 * \text{ramp}(1.24 - \text{Ti-Charge}) + 1943.36 * \text{ramp}(-0.20 - \text{HOMO}) - 3345.07 * \text{ramp}(-0.20 - \text{HOMO}) + 4.73$	0.992	0.936	168.295
<b>Eq2<sup>a</sup></b>	$\ln(\text{Activity}) = -4.91 * \text{ramp}(\text{R3 Charge} + 1.22) + 23.54 * \text{ramp}(\text{R3 Charge} + 0.13) + 33949.84 * \text{ramp}(-0.19 - \text{HOMO}) - 2361.91 * \text{ramp}(-0.20 - \text{HOMO}) + 743.80 * \text{ramp}(-0.20 - \text{HOMO}) - 33941.61 * \text{ramp}(-0.19 - \text{HOMO}) + 5.00$	0.992	0.984	230.917
<b>Eq3<sup>b</sup></b>	$\ln(\text{Activity}) = -9.15 * \text{ramp}(\text{R3 Charge} + 1.17) + 30.70 * \text{ramp}(\text{R3 Charge} + 0.24) - 257.00 * \text{ramp}(\text{HOMO} + 0.189) + 225.65 * \text{ramp}(\text{HOMO} + 0.19) - 1938.84 * \text{ramp}(-0.20 - \text{HOMO}) + 533.89 * \text{ramp}(-0.20 - \text{HOMO}) + 4.74$	0.997	0.927	564.305

<sup>a</sup> reduced Ti-charge descriptor, <sup>b</sup> deleted outliers

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