



Short communication

2D-QSAR modeling on the catalytic activities of 2-azacycyl-6-aryliminopyridylmetal precatalysts in ethylene oligomerization

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ABSTRACT

The two dimensional quantitative structure-activity relationship (2D-QSAR) approach was used to investigate the catalytic activities for a data set of 58 2-azacycyl-6-aryliminopyridylmetal complexes. Molecular descriptors were derived based on the optimized structure of complexes and selected by partial least square method (PLS). The final QSAR model containing 18 descriptors shows good predictive ability for the training set of 36 complexes ($R^2 = 0.913$, $Q^2 = 0.873$) and test set of 16 complexes ($R_c^2 = 0.971$). Then 20 new complexes were designed and predicted. The results indicate that the net charge on central metal and N atoms and also the bulky substituents are favor to the catalytic activities.

1. Introduction

The catalytic activity is one of the most crucial properties for transition metal complex catalyst in ethylene polymerization and/or oligomerization. In order to obtain highly active catalyst, diverse complex systems were designed and synthesized through modifying substituents of used ligands or with alternative ligands as well as optimized reaction conditions [1–5]. Undoubtedly, there are many achievements on the novel structure of complex from experiments [6–15], but it is still hard to predict the potential development regarding the catalytic performance of transition metal complexes.

Molecular modeling method can be used to investigate the essential mechanism during the catalytic reaction at the molecular level. In our previous studies, the catalytic activities for several transition metal complex systems were studied through correlating with effective net charge on the central metal (Q_{eff}) [16–18]. The variation trends are different, which depend on the electronic number on *d* orbital of metal atom. Besides the net charge, it was found that the LUMO-HOMO energy gap ($\Delta\epsilon$) and the energy difference among various spin states (ΔE) also exhibit certain correlation with catalytic activities [19]. Additionally, the catalytic activities were investigated from both the electronic and steric effects. By the multiple linear regressions analysis (MLRA) method, the calculated activities for iminopyridylmetal analogues show very close results to experimental data [20,21].

Quantitative structure-activity relationship (QSAR) modeling is an approach to find key descriptors between compound's micro-structure and

macro-properties. This method was proposed mainly for the field of drug discovery and proved really a powerful tool. Comparatively, its application to the polyolefin catalyst is limited. Jensen et al. [22] undertook a comprehensive 2D-QSAR study to evaluate the productivities of ruthenium metathesis catalysts. The highly specific electronic and geometric molecular descriptors give insight into the factors influenced on the catalytic activities. In their study, to eliminate the influence of the experimental conditions, the response variables were calculated from DFT instead of the experimental data. Moreover, Cruz and his coworkers introduced the 3D-QSAR approach for series of bis-cyclopentadienylZr(IV) [23], bis-dimethylsilane-indenylZr(IV) [24] and bis-indenylHf(IV) [25] metallocene catalyst systems with the data set of 7, 25 and 22 complexes, respectively. By comparative molecular field analysis (CoMFA), the results illustrate that the charge distribution around the aromatic ligands and the steric hindrance around the active site are favor to the catalytic activities. Drummond et al. performed both 2D- and 3D-QSAR approaches to investigate Ti–N=P based organometallic catalysts towards ethylene polymerization. Compared with 3D-QSAR, the fitting results for 2D model show relatively better statistical quality [26].

Generally speaking, the greater the number of the data set, the more robust and reliable the QSAR model is, while on the other hand, it becomes more difficult to get high predictive power. Herein, we show the good results by QSAR study on a data set of 58 transition metal complex precatalysts. The final QSAR model with 18 selected descriptors presents good stability and predictive power. Moreover, 20 new complexes were designed and predicted to exhibit higher catalytic activities.

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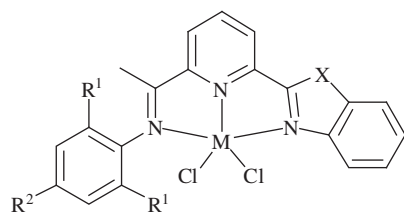
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Scheme 1. The structures of the 58 complexes and their catalytic activities in experiments.

Complex	M	X	R ¹	R ²	A _o ^a	Complex	M	X	R ¹	R ²	A _o ^a
1 ^b	Fe	NH	Me	H	172	30 ^c	Cr	O	Me	H	644
2 ^b	Fe	NH	Et	H	129	31 ^c	Cr	O	Et	H	464
3 ^b	Fe	NH	<i>i</i> Pr	H	411	32 ^c	Cr	O	<i>i</i> Pr	H	433
4 ^b	Fe	NH	Me	Me	52	33 ^c	Cr	O	Cl	H	402
5 ^b	Fe	NH	Cl	H	46	34 ^d	Cr	O	Me	Me	488
6 ^b	Fe	NH	Br	H	24	35 ^c	Cr	O	Me	Br	307
7 ^c	Co	NH	Me	H	15	36 ^d	Fe	N <i>i</i> Pr	Me	H	60
8 ^d	Co	NH	Et	H	10	37 ^c	Fe	N <i>i</i> Pr	Et	H	36
9 ^c	Co	NH	<i>i</i> Pr	H	8.7	38 ^c	Fe	N <i>i</i> Pr	<i>i</i> Pr	H	14
10 ^d	Co	NH	Me	Me	7.1	39 ^c	Fe	N <i>i</i> Pr	Cl	H	0.3
11 ^c	Co	NH	Cl	H	5.0	40 ^c	Fe	N <i>i</i> Pr	Me	Me	82
12 ^c	Co	NH	Br	H	3.6	41 ^c	Fe	N <i>i</i> Pr	Cl	H	15
13 ^c	Fe	NMe	Me	H	26	42 ^c	Co	N <i>i</i> Pr	Me	H	16
14 ^c	Fe	NMe	Et	H	22	43 ^c	Co	N <i>i</i> Pr	Et	H	11
15 ^c	Fe	NMe	<i>i</i> Pr	H	4.7	44 ^c	Co	N <i>i</i> Pr	<i>i</i> Pr	H	5.6
16 ^c	Fe	NMe	Cl	H	13	45 ^c	Co	N <i>i</i> Pr	Cl	H	6.8
17 ^c	Fe	NMe	Br	H	7.1	46 ^c	Co	N <i>i</i> Pr	Me	Me	18
18 ^c	Co	NMe	Me	H	1.2	47 ^d	Co	N <i>i</i> Pr	Me	Br	9.0
19 ^d	Co	NMe	Et	H	0.9	48 ^d	Ni	N <i>i</i> Pr	Me	H	120
20 ^d	Co	NMe	<i>i</i> Pr	H	0.5	49 ^d	Ni	N <i>i</i> Pr	Et	H	90
21 ^c	Co	NMe	Cl	H	0.3	50 ^c	Ni	N <i>i</i> Pr	<i>i</i> Pr	H	63
22 ^c	Co	NMe	Br	H	0.2	51 ^d	Ni	N <i>i</i> Pr	Cl	H	31
23 ^c	Fe	O	Me	H	68	52 ^c	Ni	N <i>i</i> Pr	Me	Me	174
24 ^c	Fe	O	Et	H	102	53 ^c	Ni	N <i>i</i> Pr	Me	Br	73
25 ^d	Fe	O	<i>i</i> Pr	H	61	54 ^c	Ni	N <i>i</i> Pr	Me	H	5.0
26 ^c	Fe	O	Cl	H	74	55 ^d	Ni	N <i>i</i> Pr	Et	H	10
27 ^d	Fe	O	Br	H	77	56 ^d	Ni	N <i>i</i> Pr	<i>i</i> Pr	H	12
28 ^d	Fe	O	Me	Me	84	57 ^c	Ni	N <i>i</i> Pr	Cl	H	31
29 ^c	Fe	O	Me	Br	19	58 ^d	Ni	N <i>i</i> Pr	Br	H	34

^a oligomerization activity: 10⁴ g·mol⁻¹·h⁻¹. ^b the outlier. ^c the training set. ^d the test set.

2. Result and discussion

An initial set of 58 2-azacycyl-6-aryliminopyridylmetal complexes for ethylene oligomerization was taken from our previous experimental works [10–15] with the structures shown in Scheme 1. These aryliminopyridyl analogues contain different substituents on the benzene ring as well as metal atoms, including Fe, Co, Ni, and Cr. Meanwhile the X atom of azacycyl substituents on the pyridine ring is varied from NH, NMe, and NiPr to oxygen. The values of the experimental catalytic activities for each complex were provided in the Table S1 along with the reaction conditions. The initial statistical analysis revealed that the complexes 1–6 decreased the quality of the model significantly, thus these six complexes were removed from the data set as outlier, leaving 52 complexes for further study.

The computational procedures, including geometry optimization of complexes, generation of molecular descriptors and also the multivariate modeling, were provided in the Supporting information in detail.

2.1. The selection of descriptors

The number of descriptors obtained by PLS-VIP variable selections was gradually decreased from 126 to 3 which were provided in Table S3. It can be seen that the value of correlation coefficient R^2 becomes lower than 0.9 when the number of descriptors is smaller than 18. Meanwhile, considering the values of cross-validation (Q^2), root mean squared error of cross-validation ($RMSEF$) and root mean squared error of cross-validation ($RMSEV$) (the detail definitions were provided in Eqs. (S2), (S3) and (S4)), the optimum results were achieved with the number of 18 descriptors. Therefore, this descriptors set was selected for the modeling study.

The information for the 18 descriptors was listed in Table 1. The descriptors were ranked from high to low according to the coefficient value of each descriptor in the final QSAR model. Meanwhile, the contributions of each descriptor to the catalytic activities were calculated by Eq. (S5) and listed together in Table 1. It is clear that the values of contribution are proportionate to the absolute values of coefficient for each descriptor.

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