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Catalytic Performance of Transition Metal Complexes in Ethylene Oligo/Polymerization by Molecular Modeling

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Introduction

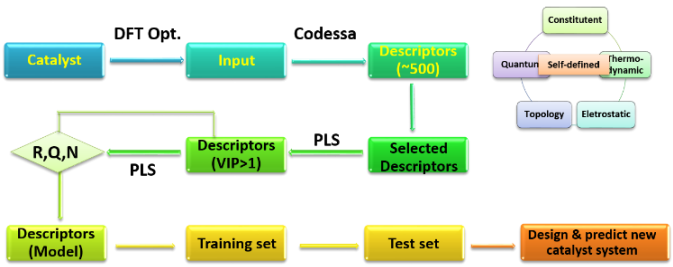
In these decades, the characteristic catalytic activities of the late transition complex catalysts towards ethylene oligo/polymerization have been attracting the attention of researchers in the field catalytic chemistry [1]. Indeed, these catalysts have high stabilities as well as high catalytic activities. In addition, they can be synthesized at low cost. By the modification of substituents on ligands as well as by the introduction of alternative ligands, a variety of the late transition complex catalysts have been synthesized for optimizing the catalytic performances for specific applications [2]. However, it is still a difficult task to predict their catalytic performance by such modification of the ligands. The molecular modeling method can be used for investigating the catalytic reaction mechanism at the molecular level and can potentially be used for predicting the catalytic activities. In our recent studies, the catalytic activities of late transition metal complex catalysts were investigated on the basis of the electronic and steric effects using the multiple linear regressions analysis (MLRA) [3] and the two dimensional quantitative structure-activity relationship (2D-QSAR) modeling [4]. Furthermore, we investigated other catalytic performances such as molecular weight and melting temperature of the obtained polymerization products by 3D-QSPR modeling and showed that good predictive and validated capabilities.

Computational Methodology

The catalytic activities of transition metal complexes were investigated by the self-defined parameters using MLRA. Based on the optimized geometry obtained by DFT calculations, two parameters representing the electronic effect, that is, the effective net charge (Q) of the metal center and the Hammett constants (F), and two parameters representing the steric effect, that is, the open cone angle (θ) and the bite angle (β), were calculated, and the catalytic activity (A) is represented using these four parameters as

$$A = m_0 + m_1F + m_2Q + m_3\theta + m_4\beta \qquad (1)$$

For the big data set of the complexes, the catalytic activities were evaluated by the 2D-QSAR modeling method with the procedure shown in Scheme 1.

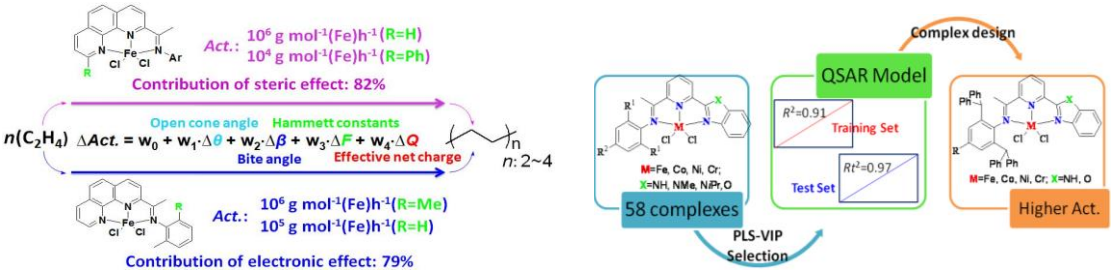


Scheme 1. The procedure of 2D-QSAR modeling method.

Results and Discussion

It has been known from experimental studies [3] that transition metal complexes systems ligated with the same ligands such as the series of 2-imino-1, 10-phenanthrolinylmetal complexes shown in Fig. 1a, exhibit a variety of different catalytic activities towards ethylene oligo/polymerization. Using the variation of the catalytic activities as a response variable and the change of the parameters as independent variables in the MLRA equation, we showed that the calculated catalytic activities exhibit a good correlation with the experimental results. The contributions in the electronic and steric effects were analyzed separately from each other to interpret the variations for their catalytic activities. It was found that the extent of the correlation among the analogues having different metal species is low compared with the extent of the correlation among the analogues having the same metal atom species.

The 2D-QSAR approach was adopted to investigate the catalytic activities for a data set of 58 2-azacyclyl-6-aryliminopyridylmetal complexes in Fig. 1b. Molecular descriptors were derived based on the optimized structure of complexes and were selected by the partial least square method (PLS). The final QSAR model containing 18 descriptors showed good predictive abilities for the training set of 36 complexes, for which the correlation coefficient value (R^2) was 0.913 and the cross validation (Q^2) was 0.873, and the test set of 16 complexes for which the correlation coefficient value (R_t^2) was 0.971. Through the detailed analysis of the relationship between the selected descriptors and the cataltyic activites, 20 new complexes were designed and their catalytic activities were predicted. The present results are expected to give guidance for the design of transition metal complex catalysts with high catalytic activities.



(a) (b)

Figure 1. The investigation of the variation of the catalytic activities for the late transition metal complexes analogues by (a) the MLRA modeling method and (b) the 2D-QSAR modeling method.

References

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