

The influence of the metal net charge of non-metallocene early transition metal catalyst on the ethylene polymerization activity

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The net charges on central metals of a serial non-metallocene early transition metal catalysts (FI catalyst) with similar steric hindrance were calculated with MM-QEq (molecular mechanism-charge equilibration) method and associated with ethylene polymerization activities of these FI catalysts. It was found that the activity increased with the net charge on metal if ignoring the influence of the steric hindrance. In other words, introduction of strong and/or more electron-withdrawing groups onto the ligand of FI catalyst would enhance the activity of the catalyst. This conclusion gave a direction to designing new FI catalyst with higher activity.

molecular mechanism, charge equilibration, FI catalyst, activity, net charge

Design and synthesis of olefin coordination polymerization catalyst are fundamental research to drive the development of polyolefin chemistry and industry. Since the discovery of olefin coordination polymerization catalyst by Ziegler in 1953, it has always been an active research subject in both academic and industrial fields. These catalysts include three categories: traditional heterogeneous Ziegler-Natta catalysts, homogeneous metallocene catalysts and non-metallocene catalysts. One of the important topics in this field is the structure-catalytic activity relationship. The exact structure of the heterogeneous Ziegler-Natta catalyst is unknown now, which mounts a huge hindrance to studying its structure-activity relationship. However, metallocene catalysts and non-metallocene catalysts are well defined organometallic complexes, so it is easy to investigate their structure-activity relationship. It is practical to adjust activity, stereospecificity and molecular weight via altering the central metal, ligand frame and the structure and position of substituent of organometallic complex. With great efforts, it has been uncovered that the main influ-

ence factors on the catalytic activity are the electronic effect of central metal and the steric effect of substituent. Möhring and Coville^[1] concluded that electronic effect could contribute 80% of the change in the polymerization activity by the influence of the steric and electronic effects on the catalytic activity of metallocene catalysts. Guo et al.^[2,3] studied some metallocene and constrained geometry catalysts using molecular mechanism (MM) and charge equilibration (QEq)^[4] method and found that catalytic activity increased with the decrease of the net charge on the central metal. Bis(imino)pyridyl Fe(II) catalyst also obeyed this inverse ratio relationship^[5]. However, direct ratio relationship occurs in salicylaldiminato Nickel(II) catalyst where activity increases with the increasing net charge^[6]. MM-QEq method establishes a quantitative correlation between activity and metal net charge of catalyst. Compared with other high

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level quantum chemistry computation methods, such as *ab initio* and DFT, MM-QEq is faster and practical in most laboratories.

In recent years, one of the frontiers of olefin coordination catalysts is non-metallocene early transition metal catalyst with phenoxy-imine or phenoxy-ketimine ligand^[7–13] (this catalyst is also called FI catalyst, the structure is showed in Figure 1). The activities of FI catalysts are very high, many of which are usually one order of magnitude higher than those of typical metallocene catalysts in the ethylene polymerization. The molecular weight of PE produced can be in a broad range via adjusting the ligand structure. Living polymerizations of ethylene and propylene can also be performed by FI catalysts^[11,12], which can be used to prepare block copolymers. In the copolymerizations of ethylene with polar comonomers, FI catalyst can keep a high activity^[14,15]. The ligands of FI catalysts are plenty. They are good model compounds to study structure-activity relationship. In this paper, we study the structure-activity relationship of FI catalysts by MM-QEq method which has not been reported up to now.

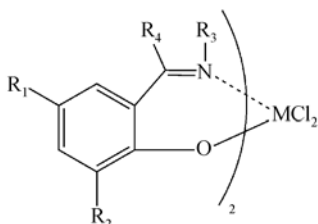


Figure 1 The structure of FI catalyst.

1 Computation method

UFF force field^[16] is used in all the geometrical optimization of FI catalysts, in which success has been obtained in salicylaldiminato Nickel(II) catalyst^[6] which has similar ligands to FI catalyst. The net charge on central metal is calculated with QEq method. Cerius² program is used in all the computation. The net charge on metal is obtained as follows: distribute the net charge to each atom and then optimize the conformer to minimize the potential energy. These two operations are circularly carried out until the potential energy of the conformer remains constant.

It is worth noting that MM-QEq is only focused on the electronic effect. However, electronic effect and steric effect will change together when a substituent changes. In order to reduce the interference of steric ef-

fect, we classed the complexes with similar steric hindrance as a group and studied their activity-net charge relationship. In fact, the activity-net charge relationship becomes unclear in comparing complexes with big difference in steric hindrance.

2 Results and discussion

2.1 The energies of the complex isomers

FI catalyst possesses octahedral coordination structure. It has five isomers according to the positions of N and O atoms, as shown in Figure 2. Two *trans* structures show no activity in ethylene polymerization because the chain propagation can not occur in the *trans* vacancy positions after elimination of two Cl atoms. The three *cis* structures could have activity. According to the crystal structures, some of FI catalysts belong to *cis*-I and some to *cis*-II. The isomer of a catalyst used in the computation is the same as its crystal structure. The *cis*-I structure is used in the unannounced catalysts. DFT calculation of complex 1 (Table 1) shows that the energy follows the

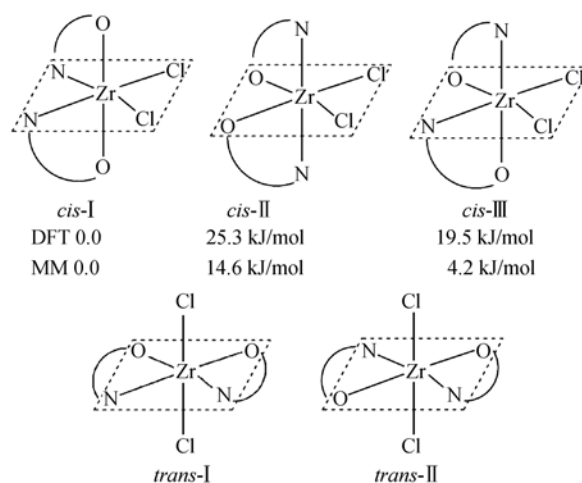


Figure 2 Five isomers of FI catalysts.

Table 1 Metal net charges and activities of complexes 1–9

Complex	R ₁	R ₂	R ₃	Net charge	Activity ^[17]
1	H	tBu	Ph	0.7084	550
2	Me	tBu	Ph	0.7054	331
3	H	tBu	2-Me-Ph	0.7036	40
4	H	tBu	4- <i>t</i> Bu-Ph	0.7097	271
5	H	tBu	3,5-di- <i>t</i> Bu-Ph	0.7035	244
6	Me	cumyl	Ph	0.6990	2096
7	Me	adamantyl	Ph	0.6986	714
8	H	Me	Ph	0.7529	0.4
9	H	iPr	Ph	0.7294	0.9

order of *cis-I*<*cis-III*<*cis-II*^[17]. MM-QEq calculation also has the same order (Figure 2), which supports that MM can be used in FI catalysts.

2.2 The net charge-activity relationship of Zr complexes

All the catalyst activities in this paper denote ethylene polymerization activities. In the following tables, the activity values cited from different references were tested in different conditions and had different units. The activities under the same conditions are comparable and those under different conditions are incomparable. The unit of activity is not listed for it is not important in comparison. The structures of complexes 1–9 (M=Zr, R₄=H) are showed in Figure 1 and the net charges and activities are listed in Table 1. Complexes 1–3 is one group, 4–5 and 6–7 are the other two groups. In each group, the steric hindrance is similar and the catalytic activity increases with the increasing net charge on Zr atom. Taking complex 1 as reference, addition of a CH₃ group on R₁ and R₃ position generates complexes 2 and 3, respectively. It can be seen that the same group CH₃ has different electron donating ability in different positions. CH₃ shows more power in R₃ position.

Comparing complexes 8 and 9, it is found that net charge is in inverse ratio to activity, which maybe results from the steric effects of Me and *i*Pr which affect activity more markedly than electronic effect here. If gathering complexes 1–9 together, the correlation between net charge and activity is poor. This phenomenon illuminates that steric effect can not be ignored in MM-QEq method used to find net charge-activity relationship.

In complexes 10–14 (Table 2, M=Zr, R₁=R₂=*t*Bu) where R₄ is aryl, when substituents vary from electron donor CH₃, H to electron acceptor F, the net charge on Zr atom and activity increase if considering complexes 10–12 as a group and 13, 11 and 14 as another group. In complexes 15–17 and 18–19 (Table 3, M=Zr, R₄=H) where R₃ is alkyl, net charge is also in direct ratio to activity. Comparing complexes 10 and 13, 12 and 14, which have the same substituents Me and F respectively at different positions, Me shows more electron-donating ability at R₃ and F also shows more electron-withdrawing ability at R₃ than at R₄. A group at R₃ has more electron effect than at R₄.

Table 2 Metal net charges and activities of complexes 10–14

Complex	R ₃	R ₄	Net charge	Activity ^[18]
10	Ph	2-Me-Ph	0.7090	3.4
11	Ph	Ph	0.7148	20.1
12	Ph	2-F-Ph	0.7519	216.3
13	2-Me-Ph	Ph	0.7081	1.7
11	Ph	Ph	0.7148	20.1
14	2-F-Ph	Ph	0.7606	33.9

Table 3 Metal net charges and activities of complexes 15–19

Complex	R ₁	R ₂	R ₃	Net charge	Activity
15	Me	<i>t</i> Bu	cyclobutyl	0.6863	22.0 ^[19]
16	H	<i>t</i> Bu	cyclobutyl	0.6876	31.6 ^[19]
17	H	<i>t</i> Bu	cyclopropyl	0.6993	50.4 ^[19]
18	H	<i>t</i> Bu	3-pentyl	0.6601	1020 ^[20]
19	H	<i>t</i> Bu	cyclohexyl	0.6804	1250 ^[20]

2.3 The net charge-activity relationship of Ti complexes

The activities of Ti complexes 20–22 (Figure 1, Table 4, M=Ti, R₄=H) increase with the increasing net charges on Ti atoms that varied with substituents on phenyl. Comparing complexes 20–22 and 3–1 which have the same ligand frames as different central metal Ti and Zr, it is found that Ti has higher net charge than Zr. As in the cases of complexes 2 and 3, in complexes 20 and 21, CH₃ in R₃ position has more electron donating effect. From complexes 23 to 25 (M=Ti, R₁=R₄=H, R₃=2,6-di-*i*Pr-Ph (Table 5), and their crystal structures are *cis-II*), the number of F atoms, the net charge on Ti atom and then the activity increase consequently. From complexes 26 to 29 (M=Ti, R₂=R₄=H, R₃=2,6-di-*i*Pr-Ph (Table 6), and their crystal structures are *cis-II*), the more the electron donating ability of the substituent, the less the net charge on Ti atom, and the less the activity of the complex. In Zn complexes 30–33 (M=Ti, R₁=R₄=H (Table 7)

Table 4 Metal net charges and activities of complexes 20–22

Complex	R ₁	R ₂	R ₃	Net charge	Activity ^[21]
20	H	<i>t</i> Bu	2-Me-Ph	0.9213	301
21	Me	<i>t</i> Bu	Ph	0.9245	1710
22	H	<i>t</i> Bu	Ph	0.9282	3240

Table 5 Metal net charges and activities of complexes 23–25

Complex	R ₂	R ₃	Net charge	Activity ^[22]
23	H	Ph	0.9800	63
24	H	2,6-di-F-Ph	1.1491	162
25	F	2,6-di-F-Ph	1.2001	194

Table 6 Metal net charges and activities of complexes 26–29

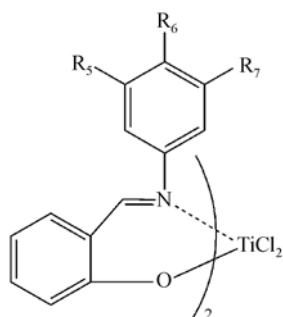
Complex	R ₁	Net charge	Activity ^[23]
26	NO ₂	0.9156	880
27	Cl	0.9153	732
28	Br	0.9147	455
29	H	0.9080	13

Table 7 Metal net charges and activities of complexes 30–33

Complex	R ₂	R ₃	Net charge	Activity ^[24]
30	tBu	(CH ₂) ₂ Ph	0.9037	890
31	tBu	(CH ₂) ₃ Ph	0.9089	1140
32	H	adamantyl	0.9202	20
33	F	adamantyl	0.9885	130

where 30–31 are a group and 32–33 are another group, and net charge is in direct ratio to activity.

With the ability or the number of electron withdrawing group increasing in complexes 34–39 (Figure 3, Table 8), the net charge on Ti atom and the activity increase.

**Figure 3** The structure of complexes 34–39.**Table 8** Metal net charges and activities of complexes 34–39

Complex	R ₅	R ₆	R ₇	Net charge	Activity ^[25]
34	H	H	H	0.9283	3580
35	H	F	H	0.9386	3960
36	F	H	F	0.9568	34800
37	F	F	F	0.9950	43300
38	H	CF ₃	H	0.9725	3600
39	CF ₃	H	CF ₃	1.007	40320

The above results prove that the ethylene polymerization activity of FI catalyst increases with the increasing

net charge on central metal. This conclusion is contrary to that obtained in metallocene and bis(imino)pyridyl Fe(II) catalysts, but is the same as that in salicylaldiminato Nickel(II) catalyst. Yang et al.^[6] explained this phenomenon with the electron number in *d* orbital of central metal. The electron configurations of Ti, Zr and Ni are 3*d*², 4*d*² and 3*d*⁸ respectively. The electron-poor Ti and Zr atoms need more electron-donating groups to decrease the positive net charge. The electron-rich Ni atom needs more electron-withdrawing groups to decrease the positive net charge. These result in less activation energy in the ethylene coordination and/or insertion and enhance the activity. However, this explanation can not be applied to FI catalysts because electron-withdrawing group is favorable to them and their metals are electron-poor Ti and Zr atoms. Ishii et al.^[25] computed the HOMO energy of ligands of complexes 34–39 using semiempirical quantum chemistry method. The results showed that the HOMO energy of ligands of complexes 34–37 and 38–39 were in direct ratio to activity respectively. However, between groups 34–37 and 38–39, the direct ratio relationship is unclear. They also considered this as steric effect. In general, the catalytic activity depends on the activation energy of olefin coordination and/or insertion. The net charge on metal should influence activation energy and then activity. The mechanism on how this happens is unknown and can not be studied by MM-QEq method.

3 Conclusion

Series of Ti and Zr FI catalysts with similar steric effect were calculated with MM-QEq method. The results indicate that the ethylene polymerization-activities of FI catalysts are in direct ratio to the net charge on central metal without consideration of steric effect. In other words, electron-withdrawing group in the ligand of a complex is favorable to the catalytic activity. This conclusion gives a direction to design new catalysts with higher activity.

- Möhring P C, Coville N J. Quantification of the influence of steric and electronic parameters on the ethylene polymerisation activity of (CpR)₂ZrCl₂/ethylaluminumoxane Ziegler-Natta catalysts. *J Mol Catal*, 1992, 77(1): 41–50[[doi](#)]
- Guo D W, Yang X Z, Liu T Q, et al. Study on the activity of constrained geometry metallocenes. *Macromol Theo Simul*, 2001, 10: 75–78[[doi](#)]

- Guo D W, Yang X Z, Yang L, et al. Molecular modeling on the prediction of silolene-bridged indenyl metallocene catalysts for isotactic polypropylene. *J Polym Sci A: Polym Chem*, 2000, 38: 2232–2238[[doi](#)]
- Rappe A K, Goddard W A. Charge equilibration for Molecular-Dynamics Simulations. *J Phys Chem*, 1991, 95(8): 3358–3363[[do](#)]
- Zhang T Z, Sun W H, Li T, et al. Influence of electronic effect on

- catalytic activity of bis(imino)pyridyl Fe(II) and bis(imino)pyrimidyl Fe(II) complexes. *J Mor Catal A-Chem*, 2004, 218(2): 119–124[[doi](#)]
- 6 Zhang T Z, Guo D W, Jie S Y, et al. Influence of electronic effect on catalytic activity of salicylaldiminato nickel(II) complexes. *J Polymr Scie A: Polym Chem*, 2004, 42(19): 4765–4774[[doi](#)]
 - 7 Makio H, Kashiwa N, Fujita T. FI catalysts: A new family of high performance catalysts for olefin polymerization. *Adv Syn Catal*, 2002, 344(5): 477–493[[doi](#)]
 - 8 Matsui S, Fujita T. FI Catalysts: Super active new ethylene polymerization catalysts. *Catal Today*, 2001, 66(1): 63–73[[doi](#)]
 - 9 Matsui S, Mitani M, Saito J, et al. Post-metallocenes: Catalytic performance of new bis(salicylaldiminato) zirconium complexes for ethylene polymerization. *Chem Lett*, 2000, 554–555
 - 10 Matsui S, Tohi Y, Mitani M, et al. New bis(salicylaldiminato) titanium complexes for ethylene polymerization. *Chem Lett*, 1999: 1065–1066
 - 11 Mitani M, Mohri J, Yoshida Y, et al. Living polymerization of ethylene catalyzed by titanium complexes having fluorine-containing phenoxy-imine chelate ligands. *J Am Chem Soc*, 2002, 124: 3327–3336[[doi](#)]
 - 12 Tian J, Hustad P D, Coates G W. A new catalyst for highly syndio-specific living olefin polymerization: Homopolymers and block copolymers from ethylene and propylene. *J Am Chem Soc*, 2001, 123: 5134–5135[[doi](#)]
 - 13 Yoshida Y, Matsui S, Fujita T. Bis(pyrrolide-imine) Ti complexes with MAO: A new family of high performance catalysts for olefin polymerization. *J Organomet Chem*, 2005, 690: 4382–4397[[doi](#)]
 - 14 Zhang X F, Chen S T, Li H Y, et al. Highly active copolymerization of ethylene with 10-undecen-1-ol using phenoxy-based zirconium/methylaluminoxane catalysts. *J Polymr Scie A: Polym Chem*, 2005, 43: 5944–5952[[doi](#)]
 - 15 Zhang X F, Chen S T, Li H Y, et al. Copolymerizations of ethylene and polar comonomers with bis(phenoxyketimine) group IV complexes: Effects of the central metal properties. *J Polymr Scie A: Polym Chem*, 2007, 45: 59–68[[doi](#)]
 - 16 Rappe A K, Casewit C J, Colwell K S, et al. Uff, a full periodic-table force-field for molecular mechanics and molecular-dynamics simulations. *J Am Chem Soc*, 1992, 114: 10024–10035[[doi](#)]
 - 17 Matsui S, Mitani M, Saito J, et al. A family of zirconium complexes having two phenoxy-imine chelate ligands for olefin polymerization. *J Am Chem Soc*, 2001, 123: 6847–6856[[doi](#)]
 - 18 Chen S T, Zhang X F, Ma H W, et al. A series of new zirconium complexes bearing bis(phenoxyketimine) ligands: Synthesis, characterization and ethylene polymerization. *J Organomet Chem*, 2005, 690: 4184–4191[[doi](#)]
 - 19 Terao H, Ishii S I, Saito J, et al. Phenoxy-cycloalkylimine ligated zirconium complexes for ethylene polymerization: Formation of vinyl-terminated low molecular weight polyethylenes with high efficiency. *Macromolecules*, 2006, 39: 8584–8593[[doi](#)]
 - 20 Bando H, Nakayama Y, Sonobe Y, et al. Bis(phenoxy-imine) Zr complexes/Et₃Al/heteropoly compound catalyst systems for ethylene polymerization. *Macromol Rap Commun*, 2003, 24: 732–736[[doi](#)]
 - 21 Furayama R, Saito J, Ishii S, et al. Ethylene and propylene polymerization behavior of a series of bis(phenoxy-imine)titanium complexes. *J Mor Catal A-Chem*, 2003, 200: 31–42[[doi](#)]
 - 22 Parssinen A, Luhtanen T, Klinga M, et al. Bis(salicylaldiminato) titanium complexes containing bulky imine substituents: Synthesis, characterization and ethylene polymerization studies. *Eur J Inorg Chem*, 2005: 2100–2109
 - 23 Sun J Q, Cheng Z Z, Nie Y J, et al. Novel titanium complexes bearing two chelating phenoxy-imine ligands and their catalytic performance for ethylene polymerization. *App Organometal Chem*, 2007, 21: 268–274[[doi](#)]
 - 24 Parssinen A, Luhtanen T, Klinga M, et al. Alkylphenyl-substituted bis(salicylaldiminato) titanium catalysts in ethene polymerization. *Organometallics*, 2007, 26: 3690–3698[[doi](#)]
 - 25 Ishii S, Saito J, Mitani M, et al. Highly active ethylene polymerization catalysts based on titanium complexes having two phenoxy-imine chelate ligands. *J Mor Catal A-Chem*, 2002, 179: 11–16[[doi](#)]