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Journal of Molecular Catalysis A: Chemical 218 (2004) 119–124

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Influence of electronic effect on catalytic activity of bis(imino)pyridyl Fe(II) and bis(imino)pyrimidyl Fe(II) complexes

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Received 2 January 2004; received in revised form 25 March 2004; accepted 25 March 2004

Abstract

The metal atom net charge correlation (MANCC) was successfully used to study the relative catalytic activities of 20 bis(imino)pyridyl Fe(II) and bis(imino)pyrimidyl Fe(II) complexes for olefins polymerization/oligomerization through modifying the Dreiding force. The net charge range on the central metal Fe was found 0.6295–0.8310, which was considered in the present study as two areas, e.g. the lower charge area (0.6295–0.7000) and the higher charge area (0.7000–0.8310). The observations reveal that the catalytic activity of bis(imino)pyridyl Fe(II) and bis(imino)pyrimidyl Fe(II) complexes does not monotonously vary with the net charge on the central metal as we found for other metal system before. There possibly is an interesting turning point around 0.7000. The activity increases with the net charge in the lower charge area, while the catalytic activity increases with reducing the net charge in the higher area. The reason that the Fe(II) catalysts possess such properties was discussed.

Keywords: Molecular mechanics; QEq charge; Bis(imino)pyridyl Fe(II) and bis(imino)pyrimidyl Fe(II) complexes; Late-transition metal catalyst; Ethylene oligomerization/polymerization

1. Introduction

Since the discovery of highly active Ni(II) and Pd(II) olefin polymerization catalysts containing α-diimine ligands by Brookhart and co-workers in 1995 [1] (Fig. 1), there is extensive study on late-transition metal catalysts in both academic and industrial research laboratories, and various late-transition metal complexes were synthesized and tested for olefins polymerization or oligomerization [2,3]. Recent advances in olefin polymerization catalysis using group 8 metals are mainly based on developments around iron, nickel and palladium catalysts. This family of catalyst has attracted great interest not only in academia but also in industry [4].

More established polymerization catalysts have been the subjects of numerous mechanistic studies based on experimental and theoretical techniques. The nature of catalytic activity is more relied on the electronic configuration of the catalyst in the ground state, especially the net charge on the central metal atom, therefore the magnitude of the net charge characterizes the activity of connecting bonds during polymerization. Möhring and Coville [5] concluded that the electronic effect could contribute as much as 80% of the change in the polymerization activities by studying the influence of the steric and electronic effect of ligands on the catalytic activity of $(CpR)_2ZrCl_2$/ethylaluminoxane. The evidences were found by us that metallocene catalyst activities increase with the reducing net charge [6,7] while the catalytic activities of α-diimine Ni(II) complexes increase along with the net charge [8]. The employed study method is to correlate the net charge on the center metal in catalyst and the catalytic activity through the combination of the charge equilibration method (QEq) [9] and molecular mechanics (MM). This method therefore could be named as the metal atom net charge correlation (MANCC) for short, which can provide a quantitative understanding of the elec-

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doi:10.1016/j.molcata.2004.03.034

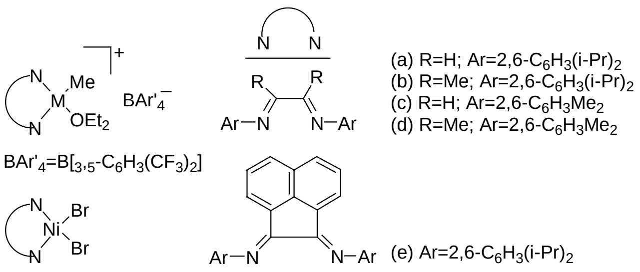


Fig. 1. Ni(II) and Pd(II) complexes with α-diimine ligands.

tronic effect and further find out different contributions of the steric effect and the electronic effect. In practice, for the relatively larger size of catalysts such as metallocenes, ab initio or DFT calculation is too demanding to be realized in general laboratory. We therefore proposed to use MANCC. It was feasible for many systems as mentioned above. Ziegler and co-workers [10] recently investigated the polymerization mechanism of the bis(imino)pyridyl Fe(II) complexes by using QM/MM method, herein we hope extend MANCC method to the type of Fe(II)-based catalysts.

In the present study, we have adjusted some empirical force field parameters employed in MM method referencing the X-ray diffraction data of bis(imino)pyridyl Fe(II). Through the charge equilibration method (QEq) we get the net charges on Fe atom of bis(imino)pyridyl Fe(II) and bis(imino)pyrimidine Fe(II) complexes, and then correlate the catalytic activities with the net charge. Results show a correlation between the net charge and the activity, but with a turning point.

2. Methods

In the studied system, there are many factors affecting the reactive performance of ethylene oligomerization over Fe(II) catalysts, such as solvent and molar ratio of catalyst to co-catalyst. It is crucial to build a simple and effective model in order to study these sophisticated systems.

Molecular models of bis(imino)pyridyl Fe(II) and bis(imino)pyrimidyl Fe(II) as individual molecule were built on Silicon Graphics O_2 workstation using the program Cerius^2 (version 4.0) developed by Molecular Simulations Incorporated (MSI).

Molecular force field forms the basis of all energy calculations for molecular mechanics (MM) and related methods. In general, a specialized force field is more accurate for predicting a limited number of structures. In comparison with other force fields (such as universal force field (UFF)) [11], the Dreiding force field [12] is capable of providing accurate geometries for a very large number of compounds with the fewest possible number of parameters. So the Dreiding force field is easier to adjust and is chosen to simulate these iron complexes. However, it does not contain any parameter for five-coordinated iron atom and is not suitable to deal with bis(imino)pyridyl Fe(II) or bis(imino)pyrimidyl Fe(II) complexes. We therefore have to modify Dreiding force field.

In terms of a set of rules in open force field of Cerius^2, regarding to element, hybridization and connectivity in Dreiding force, a new type of atom Fe5 + 2 was added. This atom type guarantees that the geometry of Fe is the same as one determined by X-ray and the formal charge is +2. To reproduce the structure of bis(imino)pyridyl Fe(II) or bis(imino)pyrimidyl Fe(II), the selected bond lengths and bond angles related with central metal, Fe5 + 2, were used in adjusting some constants in the energy expressions. For bond stretch and angle bend, harmonic function type and cosine-harmonic function type were chosen as the followings, respectively:

$$E_{\text{bond stretch}} = \frac{1}{2}K_r(r - r_0)^2$$

where K_r is the force constant, r the bond length and r_0 the equilibrated bond length.

$$E_{\text{angle bend}} = \frac{1}{2}K_\theta(\theta - \theta_0)^2$$

where K_θ is the force constant, θ the bond angle and θ_0 the equilibrated bond angle.

The regressive parameters about Fe5 + 2 were listed in Table 1.

The default cut-off value in the modified force field was 5.0 Å. Table 2 shows the comparison of the calculated data with those from X-ray diffraction on selected bond lengths and bond angles. The well consistence in Table 2 indicates that the modified force field is valid. To perform molecular mechanics calculation, all the energy terms including valence terms and non-bond terms were considered. To correlate the activity of bis(imino)pyridyl Fe(II) or bis(imino)pyrimidyl Fe(II) complexes, the charge equilibration (QEq) method was employed to obtain the net charge distributions.

The charge on Fe in their complexes was obtained: distribute the charge to each atom and then optimize the conformer to minimize the potential energy. These two operations were circularly carried out until the potential energy of the conformer remains constant.

Table 1
New parameter for the modified Dreiding force field

Bond stretch	K_r	r_0 (Å)
Fe–N_2	700.00	2.2200
Fe–N_R	700.00	2.1099
Fe–Cl	700.00	2.2720
Fe–Br	700.00	2.4420
Angle bend	K_θ	θ_0 (°)
Br–Fe–Br	100.00	110.0
Cl–Fe–Cl	100.00	111.2
N_2–Fe–Br	100.00	100.0
N_R–Fe–Br	100.00	125.0
N_2–Fe–Cl	100.00	100.0
N_R–Fe–Cl	100.00	125.0
N_2–Fe–N_2	100.00	146.1
N_2–Fe–N_R	100.00	73.0

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1**, **2** and **3**

Bond and angle	**1** (X = Cl)		**2** (X = Br)		**3** (X = Cl)	
	X-ray	MM	X-ray	MM	X-ray	MM
Fe–N(1)	2.110	2.085	2.103	2.089	2.088	2.077
Fe–N(7)	2.271	2.216	2.271	2.211	2.238	2.244
Fe–N(9)	2.266	2.216	2.260	2.211	2.250	2.244
Fe–X(1)	2.312	2.259	2.452	2.438	2.311	2.261
Fe–X(2)	2.278	2.259	2.418	2.429	2.266	2.252
N(1)–Fe–N(7)	72.7	73.7	72.8	73.6	73.2	74.2
N(1)–Fe–N(9)	73.0	74.6	72.9	73.6	72.9	74.2
N(7)–Fe–N(9)	145.5	148.3	145.4	145.6	140.1	146.3
N(1)–Fe–X(1)	118.9	122.1	118.7	118.6	94.6	112.3
N(7)–Fe–X(1)	102.4	99.7	102.5	102.3	100.6	96.3
N(9)–Fe–X(1)	96.7	98.1	97.0	96.8	102.5	101.2
N(1)–Fe–X(2)	131.3	125.1	132.3	131.2	147.9	131.9
N(7)–Fe–X(2)	97.8	98.6	98.3	96.8	98.6	96.3
N(9)–Fe–X(2)	102.3	98.3	102.0	102.3	98.9	101.2
X(1)–Fe–X(2)	109.9	112.8	109.1	110.2	117.5	115.8

3. Results and discussions

3.1. Bis(imino)pyridyl Fe(II) complexes (**1–9**) for ethylene polymerization [13] (Fig. 2)

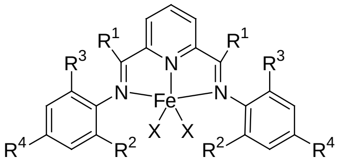
The comparison of MM data and X-ray diffraction data of complexes **1**, **2** and **3** was listed in Table 2. The maximum bond length error is 0.06 Å (Fe-N7 in complex **2**) The maximum bond angle error is 17.7° (N1-Fe-Cl1 in complex **3**). The modified Dreiding force field successfully simulated the structure of complexes **1**, **2** and **3**. The simulated structure of **1**, **2** and **3** was shown in Fig. 3. The catalytic activities of catalysts and the net charge under the same polymerization conditions were then correlated.

For complexes **1** and **2**, their structural characteristics are similar with each other. Only remarkable difference between them is halogen atom. In complex **1**, halogen atom is Cl, while halogen atom is Br in complex **2**. The higher electronegativity of Cl atom (3.16) compared with that of Br (2.96) results in that the net charge on Fe in complex **1** is larger than that in complex **2**. The anion radius of Cl^- and Br^- is respectively 1.81 and 1.95 Å. The steric effect can be excluded to most extent. The different activity mainly derived from the electronic effect. Experimentally, the catalytic activity of complex **1** is higher than that of complex **2**. When two Me groups, two i-Pr groups or one *t*-Bu was attached respectively to *o*-position of benzenyl ring, the net charge on Fe in **4**, **3** and **5** will decline due to the increasing electronic releasing ability of these group. The net charge on Fe in **4**, **5** and **3** is 0.6942, 0.6683 and 0.6536, respectively. On the whole, the catalytic activities increase with the net charge on Fe for complexes **3**, **4** and **5** under the same polymerization condition. However, there is an exception. Possibly due to the steric effect of i-Pr group, the activity of **3** is lightly higher than that of **5**.

For complexes **6**, **7**, **8** and **9**, a similar trend was also found in relation between the activity and the net charge. The activity increases approximately linearly with the net charge (Table 3).

3.2. Bis(imino)pyridyl Fe(II) complexes (**10–14**) for ethylene oligomerization [14] (Fig. 4)

When positions of substituents on aryl ring attached to the imino nitrogen were not symmetric, the oligomerization activity also increases with decreasing the net charge on Fe with the only exception of complex **12** (Table 4). The



Complex	R^1	R^2	R^3	R^4	X
1	Me	Me	Me	Me	Cl
2	Me	Me	Me	Me	Br
3	Me	i-Pr	i-Pr	H	Cl
4	Me	Me	Me	H	Cl
5	Me	t-Bu	H	H	Cl
6	H	i-Pr	i-Pr	H	Cl
7	H	Me	Me	H	Cl
8	H	Et	Et	H	Cl
9	H	Me	Me	Me	Cl

Fig. 2. Bis(imino)pyridyl Fe(II) complexes ***1–9*** for ethylene polymerization.

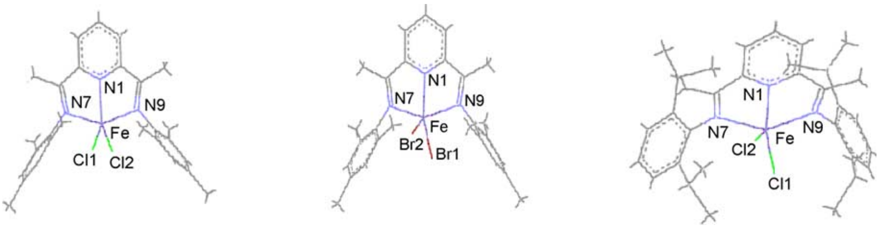
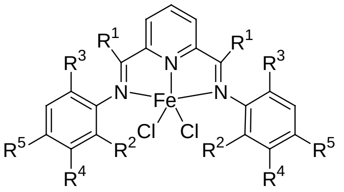


Fig. 3. Simulated molecular structures of complexes **1**, **2** and **3** (from left to right).



Complex	R^1	R^2	R^3	R^4	R^5
10	Me	Me	H	H	H
11	Me	Me	H	Me	H
12	Me	Me	H	H	Me
13	H	Me	H	H	H
14	H	1-Naphthyl			

Fig. 4. Bis(imino)pyridyl Fe(II) complexes ***10*–*14*** for ethylene oligomerization.

Table 3
Comparison of the net charge on Fe and activity for complexes **1**–**9**

Complex	Net charge	Activity (g mmol^{-1} h^{-1} bar^{-1})
1	0.6935	20600[a]
2	0.6932	17550[a]
4	0.6942	9340[b]
5	0.6683	3750[b]
3	0.6536	5340[b]
7	0.7029	560[c]
9	0.7023	550[c]
8	0.6718	340[c]
6	0.6635	305[c]

Polymerization conditions: co-catalyst MAO, isobutane solvent, 10 bar of ethylene, reaction time 1 h.

[a] Molar ratio of Fe/Al for **1** and **2** is 1000, $AlEt_3$ as the scavenger, reaction temperature 35 °C.

[b] Molar ratio of Fe/Al for **3**, **4** and **5** is 1000, $Al(i\text{-}Bu)_3$ as the scavenger, reaction temperature 50 °C.

[c] Molar ratio of Fe/Al for **6**, **7**, **8** and **9** is 200, $AlEt_3$ as the scavenger, reaction temperature 35 °C.

typical example is the significant comparison of complexes **10** and **13**. In complex **10**, the electronic releasing ability of Me groups attached to imino carbon results to the lower net charge (0.7053) compared with that (0.7143) of complex **13**. The relative order of catalytic activity is on contrary to that of the net charge on Fe. Namely, the ketimine-based Fe displaced the relatively higher activities than their analogous aldimine-based Fe catalysts under the same conditions. The same result (such as complexes **4** and **7**) also can be found in Section 1.

*3.3. F-containing bis(imino)pyridyl Fe(II) complexes (**15**–**17**) for ethylene oligomerization [15] (Fig. 5)*

The simulated structure of complex **16** was showed in Fig. 6. The comparison of simulated structure data and X-ray data was listed in Table 5.

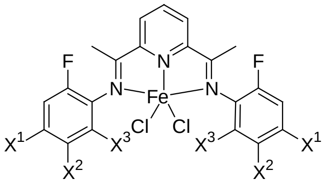
Table 4
The comparison of the net charge on Fe and catalytic activity for complexes **10**–**14**

Complex	Net charge	Activity (g mmol^{-1} h^{-1} bar^{-1})
14	0.7166	230
13	0.7134	480
10	0.7053	1300
12	0.7044	1040
11	0.7014	2570

Polymerization condition: ethylene pressure 5 bar, reaction temperature 50 °C, reaction time 1 h, co-catalyst MAO, Al/Fe 1000, solvent isobutane.

Table 5
Simulated structural data and X-ray data for complex **16**

Bond and angle	X-ray	MM
Fe–N(2)	2.0760	2.1099
Fe–N(1)	2.2190	2.2110
Fe–N(3)	2.2190	2.2330
Fe–Cl(1)	2.2630	2.2915
Fe–Cl(2)	2.2590	2.2771
N(2)–Fe–Cl(1)	118.8	119.1
N(2)–Fe–Cl(2)	131.1	129.6
Cl(1)–Fe–Cl(2)	110.1	111.3
N(2)–Fe–N(1)	74.7	73.0
N(2)–Fe–N(3)	74.7	73.1
N(1)–Fe–N(3)	148.0	146.1
Cl(1)–Fe–N(1)	101.2	100.6
Cl(1)–Fe–N(3)	96.7	96.8
Cl(2)–Fe–N(1)	96.7	97.5
Cl(2)–Fe–N(3)	101.2	103.0



Complex	X^1	X^2	X^3
15	H	H	F
16	H	F	H
17	F	H	H

Fig. 5. F-substituted bis(imino)pyridyl Fe(II) complexes ***15*–*17***.

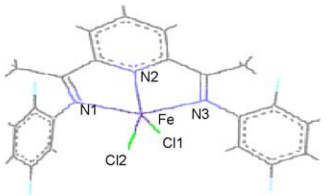
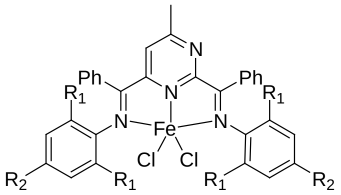


Fig. 6. Simulated molecular structures of complex **16**.

Table 6
The comparison of the net charge on Fe and catalytic activity for complexes **15**–**17**

Complex	Net charge	Activity (g mmol^{-1} h^{-1})
15	0.8310	4.07×10^4
17	0.7865	1.11×10^5
16	0.7549	9.33×10^4

Polymerization conditions: pressure of ethylene is 10 atm, Fe(II) catalyst 0.6 μmol, co-catalyst MMAO 0.6 mmol, molar ratio of Al/Fe 1000, reaction temperature 60 °C, solvent toluene, reaction time 15 min.



Complex	R^1	R^2
18	Me	H
19	Me	Me
20	i-Pr	H

Fig. 7. Bis(imino)pyrimidyl Fe(II) complexes ***18–20***.

Due to the stronger electronic drawing ability of F atom, the net charge on Fe is increased remarkably (Table 6). The electronic drawing ability of F atom on *p*-position in complex **17** is stronger than that of one on *m*-position in complex **16** while two F atoms on *o*-position has the strongest electron drawing ability in complex **15**. The net charge on Fe atom in complexes **15**, **16** and **17** should increase in the such order: ***16*** < ***17*** < ***15***. So the net charge on Fe in complex **15** is the highest (0.8310). The calculation result confirms the analysis in view of organic chemistry. Experimentally, complex **15** conversely showed the lowest activity. The activity of **15** is lower than that of **16** or **17**. Approximately, the catalytic activity increases with the reducing net charge for these three complexes **15–17**.

3.4. Bis(imino)pyrimidine Fe(II) complexes (18–20) for ethylene polymerization [16] (Fig. 7)

With the increase of the number and the electron-releasing ability of the substituents on the aryl ring, the charge on Fe should decline correspondingly in the order: ***18*** > ***19*** > ***20***. This estimation is completely in accordance with QEq calculations. The correlation showed that the catalytic activity nearly increases with the net charge on Fe (Table 7).

3.5. Analysis of reason of the relation between the net charge and the catalytic activity of Fe(II) catalysts

According to the above correlation of the catalytic activity and the net charge on Fe, it is very clear that the catalytic activity of bis(imino)pyridyl Fe(II) complexes and bis(imino) pyrimidine Fe(II) complexes is obviously influenced by the net charge on the central metal Fe. When the net charge on Fe (for complexes **1–9** and **18–20**) is less than 0.7000, the activity increases with the net charge on the central metal Fe. However, if the net charges increase progressively to exceed 0.7000, the activity will conversely drop (such as complexes **10–17**) with the increasing charge (Fig. 8).

Table 7
Comparison of the net charge on Fe and activity for complexes **18–20**

Complex	Net charge	Activity ($g\,mmol^{-1}\,h^{-1}\,bar^{-1}$)
18	0.6909	3550
19	0.6905	3850
20	0.6295	490

Polymerization conditions: solvent is isobutane, molar ratio of Fe/Al is 0.5/1000, reaction temperature 50 °C, reaction time 1 h, pressure of ethylene 4 bars.

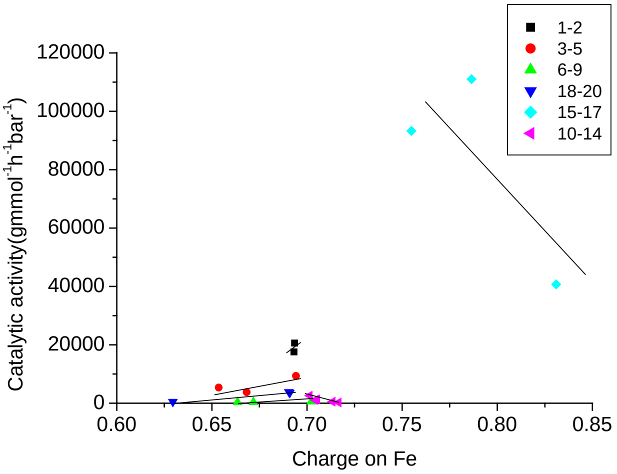


Fig. 8. Comparison between the net charge and the catalytic activity for complexes **1–20**.

In the previous study [6,7], it was found that the polymerization activity of early-transition metal complexes (such as titanium and zirconium ferrocenes) increases with the reducing net charge on the central metal. Such observations completely obey with Olive's concept [17]: the better electron donor will reduce the positive charge on the metal and thereby weaken the excessively stable bonding between Ti(Zr) and R (growing chain). The Ti(Zr)–R bond will become more active.

However, for late-transition metal catalysts, α-diimino Ni (II) complexes [8], the catalyst activity increases with the net charge on the central metal. Such observations support also the Olive's concept in another viewpoint. According to Olive, M–R bond must have just the correct stability. The excessively stable or unstable M–R is undesirable for the catalytic activity. Increasing the net charge on central metal Ni is helpful for improvement of the excessively unstable Ni–R bond.

The reason for the formation of the excessively unstable Ni–R and stable Ti(Zr)–R bonds possibly result mainly from the different d-orbital configuration. Ni holds $3d^8$ configuration while Ti and Zr do respectively $3d^2$ configuration. Ni is electron-rich compared with early-transition metals Ti and Zr. Therefore Ti(Zr)–R bond was considered too stable to be inserted easily by coordinated ethylene while Ni–R bond is too unstable to by the insertion of ethylene. The very fine adjustment of the stability of M–R bonds is obviously necessary. For Ti(Zr) catalysts, to reduce the positive charge (or electrophilicity) of the center metal is to increase the catalytic activity. So the polymerization activity of Ti(Zr) catalysts increases with the reducing net charge on the center metal. On the contrary, the polymerization activity of Ni catalysts increases with the net charge on the center metal.

Pauling cation radius of Ti^{4+}, Fe^{2+} and Ni^{2+} is 0.68, 0.75 and 0.70 Å, respectively. The cation radius of Fe^{2+}

is similar with that of Ti^{4+} and Ni^{2+}. However, Fe(II) holds $3d^6$ electron configuration that is typically neither electron-rich (like Ni atom $3d^8$) nor electron-poor (like Ti and Zr $3d^2$). The d-orbital electron characters make polymerization properties of iron(II) catalysts actually lie between that of the early-transition metal catalysts and that of the late-transition metal catalysts. Therefore the catalytic activity of bis(imino)pyridyl Fe(II) and bis(imino)pyrimidyl Fe(II) complexes does not always vary monotonously with the net charge. There appears a turning point of the charge variation that makes iron(II) catalyst perform not only like nickel(II) catalyst but also like a little these early-transition metal catalyst (such as Ti or Zr catalysts).

The relation between the net charge and the catalytic activity of iron (II) catalyst is similar with that of nickel(II) in the lower charge area because of the too unstable Fe–R bond. So the catalytic activities increase with the net charge. However, too large net charge means the excessively stable Fe–R bond in the higher charge area. Therefore the activity drops with the increasing charge. The further experiment and quantum calculations have to be undertaken to understand the result of the adjustment of Fe–R bond grade.

4. Conclusions

A new type of atom Fe5 + 2 was added in the modified Dreiding force field with some adjusted constants in the energy expressions of bond stretch and angle bend. As a result, the molecular structures of five-coordinate iron(II) complexes were successfully simulated with the maximum bond length error of 0.06 Å and the maximum bond angle error of 17.7°.

Analysis of the relation between the net charge on iron(II) atom and the catalytic activity of twenty bis(imino)pyridyl and bis(imino) pyrimidine Fe(II) complexes for ethylene polymerization or oligomerization indicates that the adjustment of activity of Fe(II) catalysts are more distinguished from that of nickel(II) catalysts due to the $3d^6$ electron configuration of iron(II). There exits an interesting turning point for the net charge versus the activity curve. The result leads to an un-monotonous relation of the net charge and the activity for iron(II) catalysts.

Acknowledgements

We are grateful to the Chinese Academy of Sciences for financial supports under the Fund of One Hundred Talents, and the National Natural Science Foundation of China, National Natural Science Foundation of China No. 20272062, and X. Yang to NSFC No. 20074041, 863 High Technology Project (2002AA333060), and Special Funds for Major State Basic Research Project (G19990648 00).

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