

Feature Article

PROSPECTS AND CRUCIAL PROBLEMS IN OLIGOMERIZATION AND POLYMERIZATION WITH IRON AND COBALT COMPLEX CATALYSTS

Su-yun Jie

*State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering,
Zhejiang University, Hangzhou 310027, China*

Wen-hua Sun* and Tianpengfei Xiao

*Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100190, China*

Abstract The discovery of highly active 2,6-bis(imino)pyridyl iron and cobalt complexes provided a milestone of late-transition metal catalysts for ethylene oligomerization and polymerization with being currently investigated for the scale-up process. The crucial problems are remaining in the catalytic systems: the catalytic systems targeting ethylene polymerization produce more oligomers at elevated reaction temperatures, however, there is a recognizable amount of high-molecular-weight polyethylene remained in the modified catalytic system for the oligomerization process. Beyond the modification of bis(imino)pyridyl metal complexes, several alternative procatalysts' models have been developed in our group. This review highlighted the achievements in exploring new iron and cobalt complexes with tridentate NNN ligands as procatalysts for ethylene oligomerization and polymerization.

Keywords: Iron complex; Cobalt complex; Ethylene oligomerization; Ethylene polymerization.

INTRODUCTION

The discovery of new cationic Pd(II) and Ni(II) catalysts with α -diimine ligands for ethylene polymerization rejuvenated the era of late transition metal catalysts for the oligomerization and polymerization of ethylene, α -olefins and cyclic olefins^[1]. Subsequent iron and cobalt procatalysts with 2,6-bis(arylimino)pyridine ligands developed simultaneously by Brookhart^[2, 3] and Gibson^[4] were remarkably productive for ethylene oligomerization and polymerization. Because of the advantages of iron and cobalt catalysts, such as lower toxicity, high catalytic activity and high α -olefin selectivity, the related papers have mushroomed concerning the effects of ligand modifications and the design of alternative catalysts' models. There are several comprehensive reviews nicely summarizing their related progressive works^[5–10]. Moreover, industrial motivations have been made by joint adventures of DuPont and PetroChina for ethylene oligomerization, and BP for ethylene polymerization targeting high density polyethylene (HDPE) with the assistance of Albemarle. However, these processes commonly happened with both ethylene oligomerization and polymerization; the oligomers would be byproducts in the process for HDPE, whilst the pipeline of catalytic system was possibly stopped with high-molecular-weight PE (even in a quite small amount) within the catalytic system for ethylene oligomerization.

Though many alternative iron and cobalt complexes showed lower catalytic activity in comparison with those ligated by bis(imino)pyridine ligands, we have enduringly worked on designing new tridentate NNN

* Corresponding author: Wen-hua Sun (孙文华), E-mail: whsun@iccas.ac.cn

Received March 8, 2010; Revised March 19, 2010; Accepted March 20, 2010
doi: 10.1007/s10118-010-0034-6

ligands and their iron and cobalt complexes for new catalysts' models. Fortunately, several models have been established and proved to be successful, including ligands of 6-organyl-2-(imino)pyridines, 2-imino-1,10-phenanthrolines, 2,8-bis(imino)quinolines *et al.* Herein we illustrate these model precatalysts and discuss their prospects and critical problems regarding ethylene oligomerization and polymerization.

FROM 2,6-BIS(IMINO)PYRIDINES TO FRAMEWORKS OF 1,10-PHENANTHROLINE DERIVATIVES

Regarding catalysts containing 2,6-bis(imino) pyridines, iron complexes (**1**, Fig. 1) containing both symmetrical and unsymmetrical ligands were employed in our group^[11]. Due to high price of diacetylpyridine, an easy synthetic procedure was developed by us with getting a new precursor of 6-acetylpyridine-2-carboxylate^[12], and the iron and cobalt complexes ligated by 2-(ethylcarboxylato)-6-iminopyridines (**2**, Fig. 1)^[13] exhibited good activities for oligomerization and polymerization with high selectivity for linear α -olefins in the presence of methylaluminoxane (MAO) as cocatalyst.

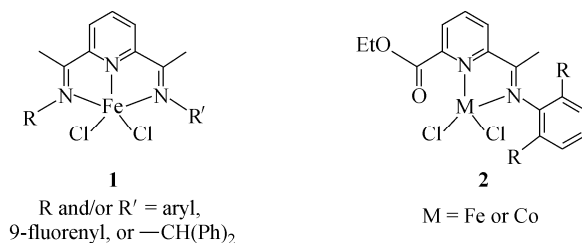


Fig. 1 Precatalysts based on iminopyridine ligands

Inspired by 2,6-bis(imino)pyridine systems, metal complexes (**3**, Fig. 2) containing 2,9-bis(imino)-1,10-phenanthroline ligands were synthesized^[14], however, the iron complexes **3** showed only negligible activities for ethylene polymerization. Interestingly, the cobalt complexes **3** showed good activity for ethylene oligomerization and polymerization (up to $9.3 \times 10^5 \text{ g mol}^{-1} \text{ h}^{-1}$). The considerable reason was the additional nitrogen of the second imino group in iron system which may occupy the necessary site for the coordination of ethylene^[15, 16]. To verify this hypothesis, the 2-imino-1,10-phenanthroline ligands and their corresponding complexes (**4**, Fig. 2) were synthesized^[17, 18], and the iron complexes **4** showed high catalytic activities for ethylene oligomerization with high selectivity for α -olefins. Parallel cobalt analogues **4** were also investigated with good catalytic activities^[19]. Beyond ours, the derivatives of cobalt catalysts were also reported by Solan's group^[20].

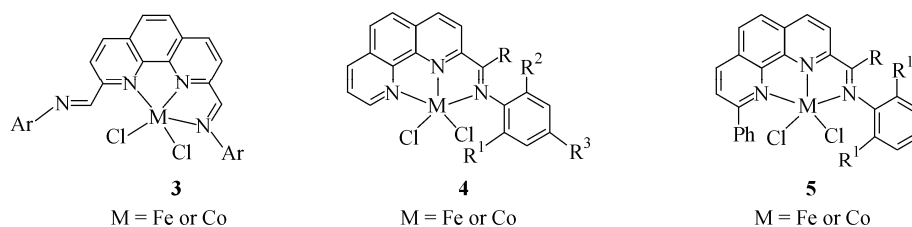


Fig. 2 Precatalysts based on iminophenanthrolines

Regarding the steric and electronic effects of ligands, 2-imino-9-phenyl-1,10-phenanthroline metal complexes (**5**, Fig. 2) were prepared and showed lower activities^[21] in comparison with the model **4**^[17, 18]. The presence of a phenyl group at the 9-position may hinder the insertion of ethylene. In addition, the replacement of

the imino group by a benzimidazole, benoxazole or oxazoline group provided new iron and cobalt complexes **6–8** (Fig. 3)^[22, 23]. On treatment with modified methylaluminoxane (MMAO), these procatalysts could oligomerize ethylene to dimers and trimers with good activities and good selectivity of α -olefins. Higher activity and better selectivity for 1-butene could be obtained under higher ethylene pressure and reaction temperature.

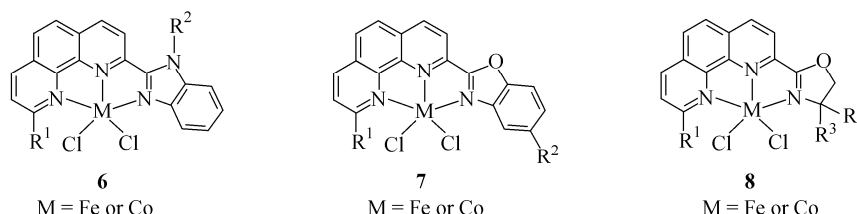


Fig. 3 Procatalysts based on heterocyclophenanthrolines

2-(2-BENZIMIDAZOLYL)-6-(1-(ARYLIMINO)ETHYL)PYRIDINES

Though the majority of 2-organylimino-pyridinyl ligands had been reported^[9], the designing of new iminopyridyl-based ligands is targeting for alternative catalysts' models. Among the possible structural variations of the 2,6-bis(arylimino)pyridyl moiety, it has been attractive in using the N-heterocycles to replace one imine group in 2,6-bis(arylimino)pyridines. Therefore, the iron and cobalt complexes (**9**, Fig. 4) containing 2-(1H-2-benzimidazolyl)-^[24], 2-(1-methyl-2-benzimidazolyl)-^[25] and 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino) ethyl)pyridines^[26] were synthesized and used as procatalysts for ethylene oligomerization and polymerization. In the presence of either MAO or MMAO, these procatalysts **9** performed good showing high catalytic activities ($1.43 \times 10^7 \text{ g mol}^{-1} \text{ h}^{-1}$) in producing α -olefins (C₄–C₂₈) with high selectivity, moreover, some waxes were also obtained by cases. In a typical example, the iron complex with a remaining N–H group on the benzimidazole showed higher activity than its analogues with alkylated benzimidazoles^[24]. Their cobalt analogues **9** showed moderate catalytic activities for ethylene oligomerization.

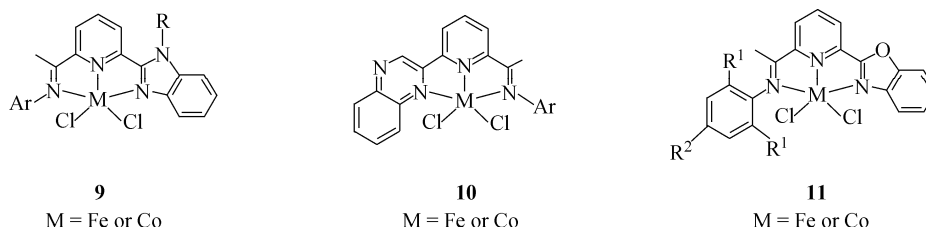


Fig. 4 Procatalysts based on heterocyclopyridines

6-(QUINOXALIN-3-YL)-2-(1-(ARYLIMINO)ETHYL)PYRIDINES

Iron and cobalt complexes (**10**, Fig. 4) bearing 6-(quinoxalin-3-yl)-2-iminopyridines were also synthesized and evaluated for ethylene reactivity^[27]. Initially scanning with cocatalysts of Et₂AlCl, MMAO or MAO, the iron procatalysts **10** performed the best activities with MAO for ethylene oligomerization, and butenes were observed as the major products. It was necessary to conduct ethylene oligomerization at lower temperature for high activities because of the thermal instability for active species. Increasing ethylene pressure, both activity and content of longer-chain oligomers increased. However, MMAO was approved as the most suitable cocatalyst in the catalytic system by their cobalt analogues **10**, displaying moderate to good catalytic activities for ethylene oligomerization (butenes as the major products). In the catalytic model **10**, the iron procatalysts showed better activities than their cobalt analogues.

2-(2-BENZOXAZOLYL)-6-(1-(ARYLIMINO)ETHYL)PYRIDINES

Benzoxazole as an important N-heterocycle compound was also of great interest to replace one imino group to form ligands of 2-(2-benzoxazolyl)-6-(1-(arylimino) ethyl)pyridines. The metal complexes of 2,6-bis(2-oxazolyl)pyridines by Nomura showed moderate activity for olefin polymerization^[28, 29]. Replacing one of the imino groups in 2,6-diiminopyridines with a benzoxazolyl group resulted in the formation of 2-(benzoxazolyl)-6-[1-(arylimino)-ethyl]pyridines^[30]. Their metal complexes (**11**, Fig. 4) formed a new type of readily accessible ethylene oligomerization catalysts^[31]. Whereas AlEt₃ and Et₂AlCl proved to be ineffective cocatalysts, activation with MMAO gave activities of up to 1 g mol⁻¹ h⁻¹ Pa⁻¹ for ethylene polymerization and 13 g mol⁻¹ h⁻¹ Pa⁻¹ for oligomerization. α -Olefins obtained were in the range of C₄–C₂₈, with high selectivity for terminal unsaturated olefins. Raising the reaction temperature resulted in an obvious decrease in productivity and selectivity for α -olefins.

With MAO as cocatalyst at 1.01 MPa of ethylene, the cobalt procatalysts **11** showed improved activities^[32] in comparison with their analogues ligated by 2-(benzimidazolyl)-6-iminopyridines^[25, 26]. These cobalt procatalysts **11** showed an unique behavior depending on the reaction temperature^[32]: at room temperature only ethylene oligomerization was observed, giving 1-alkenes with high selectivity, whilst at elevated temperatures polyethylenes were only produced. The catalytic system was believed as the first temperature-switch cobalt procatalyst in the oligomerization and polymerization of ethylene, which provides the possibility of practical application.

LIGANDS WITH QUINOLINE FRAMEWORK

Extensively, the iron and cobalt complexes (**12**, Fig. 5) bearing *N*-((pyridin-2-yl)methylene)-8-aminoquinolin derivatives were formed^[33]. Activated with MMAO, iron complexes **12** exhibited high catalytic activities up to 10⁶ g mol⁻¹ h⁻¹ for ethylene oligomerization with dimers and trimers as products, their cobalt analogues also showed good catalytic activity. Ligands with more bulky substituents enhanced the activities of their Fe(II) procatalysts, however, ligands containing less bulky substituents resulted in better activities of their cobalt analogues. Therefore, the tridentate ligands could finely tune the catalytic activities of their metal complexes, therefore, derivative ligands with alternative substituents are worthy of further investigation for highly active species.

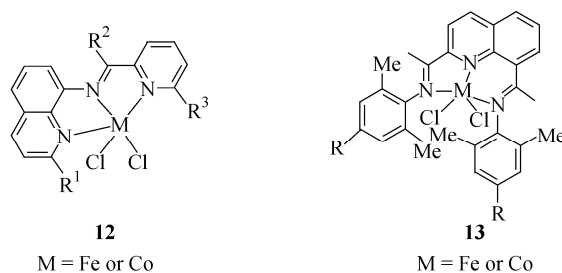


Fig. 5 Procatalysts based on quinoline derivatives

Very recently, a series of iron and cobalt complexes (**13**, Fig. 5) bearing 2,8-bis(1-aryliminoethyl)quinolines were prepared^[34], activated with MAO, they showed the unique property towards ethylene polymerization: no activity observed at low temperatures, but high activity achieved at temperatures higher than 80°C (up to 7.61 × 10⁶ g mol⁻¹ h⁻¹ at 100°C). This illustrated the stable active species at higher reaction temperatures. Moreover, the polyethylenes obtained were high-molecular-weight with narrow molecular weight distribution. This is the first example of iron and cobalt procatalysts to perform high activity for ethylene polymerization at high temperatures.

CONCLUSIONS AND PROSPECTS

The iron and cobalt procatalysts bearing tridentate ligands are promising for ethylene oligomerization due to the advantages as high activity and high selectivity for linear α -olefins; whilst polyethylenes obtained in the polymerization provided unique materials with long-chain vinyl-type linearity. Beyond bis(imino)pyridyl iron and cobalt procatalysts, there are more alternative models of procatalysts showing high activity and selectivity. Especially, several catalysts' models showed high activity in ethylene oligomerization with high selectivity for α -olefins. Though some amounts of polyolefin waxes were observed, the process using such catalysts is promising because of such waxes without high molecular fractions. In general, any polyolefins with high-molecular-weight could potentially block the pipelines of ethylene oligomerization process. In addition, the practical advantages of iron and cobalt procatalysts are the easy synthesis, relative stability and lower toxicity.

A critical problem exists commonly in the catalysis of late-transition metal catalysts for ethylene polymerization: elevating reaction temperature usually leads to chain transfers increased and chain propagations hindered, resulting products with lower molecular weights (such as polyethylene waxes or oligomers). The recent procatalysts provided some possibilities to solve this problem. The cobalt procatalyst **11** with 2-(benzoxazolyl)-6-[1-(arylimino)-ethyl]pyridines only produced polyethylene at elevated temperatures^[32], the procatalysts **13** showed high activity for ethylene polymerization to produce polyethylenes with high-molecular-weight and relatively narrow molecular weight distributions at 80–100°C^[34]. With the best of our knowledge, this is the first example that iron catalyst maintains high activity for ethylene polymerization without oligomerization at the commercial operating temperature (about 80°C for Ziegler-Natta catalytic system), though a few iron complexes ligated by modified bis(imino)pyridines were still highly active for ethylene oligomerization along with polymerization^[35].

Additionally, versatile ligands are interesting in developing new iron and cobalt procatalyst for ethylene oligomerization and polymerization. The development of new catalysts' models will rely on more works of organic synthesis, coordination, structural and physical chemistry, and catalytic parameters would be finely controlled. Further investigations are worthy to carry out for academic consideration and industrial processes.

REFERENCES

- 1 Johnson, L.K., Killian, C.M. and Brookhart, M., *J. Am. Chem. Soc.*, 1995, 117(23): 6414
- 2 Small, B.L., Brookhart, M. and Bennett, A.M.A., *J. Am. Chem. Soc.*, 1998, 120(16): 4049
- 3 Small B.L. and Brookhart, M., *J. Am. Chem. Soc.*, 1998, 120(28): 7143
- 4 Gibson, V.C., Kimberley, B.S., White, A.J.P., Williams, D.J. and Howard, P., *Chem. Commun.*, 1998, (3): 313
- 5 Gibson, V.C., Redshaw, C. and Solan, G.A., *Chem. Rev.*, 2007, 107(5): 1745
- 6 Bianchini, C., Giambastiani, G., Rios, I.G., Mantovani, G., Meli, A. and Segarra, A.M., *Coord. Chem. Rev.*, 2006, 250(11–12): 1391
- 7 Gibson V.C. and Spitzmesser, S.K., *Chem. Rev.*, 2003, 103(1): 283
- 8 Ittel, S.D., Johnson, L.K. and Brookhart, M., *Chem. Rev.*, 2000, 100(4): 1169
- 9 Bianchini, C., Giambastiani, G., Luconi, L. and Meli, A., *Coord. Chem. Rev.*, 2010, 254(5–6): 431
- 10 Sun, W.H., Zhang, S. and Zuo, W., *C. R. Chim.*, 2008, 11(3): 307
- 11 Ma, Z., Sun, W.H., Li, Z.L., Shao, C.X., Hu, Y.L. and Li, X.H., *Polym. Int.*, 2002, 51(10): 994
- 12 Asma, M., Adewuyi, S., Kuang, X., Badshah, A. and Sun, W.H., *Lett. Org. Chem.*, 2008, 5(4): 296
- 13 Sun, W.H., Tang, X.B., Gao, T.L., Wu, B., Zhang, W.J. and Ma, H.W., *Organometallics*, 2004, 23(21): 5037
- 14 Wang, L., Sun, W.H., Han, L., Yang, H., Hu, Y. and Jin, X., *J. Organomet. Chem.*, 2002, 658(1–2): 62
- 15 Britovsek, G.J.P., Baugh, S.P.D., Hoarau, O., Gibson, V.C., Wass, D.F., White, A.J.P. and Williams, D.J., *Inorg. Chim. Acta.*, 2003, 345: 279
- 16 Ameerunisha, S., Schneider, J., Meyer, T., Zacharias, P.S., Bill, E. and Henkel, G., *Chem. Commun.*, 2000, (21): 2155

- 17 Jie, S., Zhang, S., Sun, W.H., Kuang, X., Liu, T. and Guo, J., *J. Mol. Catal. A: Chem.*, 2007, 269(1-2): 85
- 18 Sun, W.H., Jie, S., Zhang, S., Zhang, W., Song, Y., Ma, H., Chen, J., Wedeking, K. and Fröhlich, R., *Organometallics*, 2006, 25(3): 666
- 19 Jie, S., Zhang, S., Wedeking, K., Zhang, W., Ma, H., Lu, X., Deng, Y. and Sun, W.H., *C.R. Chim.*, 2006, 9(11-12): 1500
- 20 Pelletier, J.D.A., Champouret, Y.D.M., Cadarso, J., Clowes, L., Gañete, M., Singh, K., Thanarajasingham, V. and Solan, G.A., *J. Organomet. Chem.*, 2006, 691(19): 4114
- 21 Jie, S., Zhang, S., and Sun, W.H., *Eur. J. Inorg. Chem.*, 2007, (35): 5584
- 22 Zhang, M., Hao, P., Zuo, W., Jie, S. and Sun, W.H., *J. Organomet. Chem.*, 2008, 693(3): 483
- 23 Zhang, M., Gao, R., Hao, X. and Sun, W.H., *J. Organomet. Chem.*, 2008, 693(26): 3867
- 24 Xiao, L., Gao, R., Zhang, M., Li, Y., Cao, X. and Sun, W.H., *Organometallics*, 2009, 28(7): 2225
- 25 Sun, W.H., Hao, P., Zhang, S., Shi, Q., Zuo, W., Tang, X. and Lu, X., *Organometallics*, 2007, 26(10): 2720
- 26 Chen, Y., Hao, P., Zuo, W., Gao, K. and Sun, W.H., *J. Organomet. Chem.*, 2008, 693(10): 1829
- 27 Sun, W.H., Hao, P., Li, G., Zhang, S., Wang, W., Yi, J., Asma, M. and Tang, N., *J. Organomet. Chem.*, 2007, 692(21): 4506
- 28 Nomura, K., Sidokmai, W. and Imanishi, Y., *Bull. Chem. Soc. Jpn.*, 2000, 73(3): 599
- 29 Nomura, K., Warit, S. and Imanishi, Y., *Macromolecules*, 1999, 32(14): 4732
- 30 Gao, R., Zhang, M., Liang, T., Wang, F. and Sun, W.H., *Organometallics*, 2008, 27(21): 5641
- 31 Gao, R., Li, Y., Wang, F., Sun, W.H. and Bochmann, M., *Eur. J. Inorg. Chem.*, 2009, (27): 4149
- 32 Gao, R., Wang, K., Li, Y., Wang, F., Sun, W.H., Redshaw, C. and Bochmann, M., *J. Mol. Catal. A: Chem.*, 2009, 309(1-2): 166
- 33 Wang, K., Wedeking, K., Zuo, W., Zhang, D. and Sun, W.H., *J. Organomet. Chem.*, 2008, 693(6): 1073
- 34 Zhang, S., Sun, W.H., Xiao, T., and Hao, X., *Organometallics*, 2010, 29(5): 1168
- 35 Ionkin, A.S., Marshall, W.J., Adelman, D.J., Fones, B.B., Fish, B.M. and Schiffhauer, M.F., *Organometallics*, 2008, 27(6): 1147