Journal of Molecular Catalysis A: Chemical 160 (2000) 243–247

www.elsevier.com/locate/molcata

Ethylene oligomerization by diimine iron(II) complexes/EAO

Qian Mingxing, Wang Mei, He Ren *

Open Laboratory of Comprehensive Utilization for Carbon Resources, Dalian University of Technology,
Dalian 116012, People's Republic of China

Received 8 February 2000; accepted 17 March 2000

Abstract

The catalytic properties of a series of Fe(II) diimine complexes (diimine = N,N'-*o*-phenylenebis(salicylideneaminato), N,N'-ethylenebis(salicylideneaminato), N,N'-*o*-phenylenebisbenzal, N,N'-ethylenebisbenzal) in combination with ethylaluminoxane (EAO) for ethylene oligomerization have been investigated. Treatment of the iron(II) complexes with EAO in toluene generates active catalytic systems in situ that oligomerize ethylene to low-carbon olefins. The effects of reaction temperature, ratios of Al/Fe and reaction periods on catalytic activity and product distribution have been studied. The activity of complex $FeCl_2(PhCH{=}o\text{-}NC_6H_4N{=}CHPh)$ with EAO at 200°C is 1.35×10^5 g oligomers/mol Fe · h, and the selectivity of C_{4-10} olefins is 84.8%. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ethylene oligomerization; Iron complexes; Ethylaluminoxane

1. Introduction

Low-carbon linear α-olefins are used primarily as comonomers for production of linear low-density polyethylene, plasticizers and synthetic lubricants. Catalysts of ethylene oligomerization now used in industry include neutral Ni(II) complexes bearing bidentate monoanionic ligands that are the basis for the Shell High Olefin Process (SHOP) [1–3], and aluminum alkyls, which find utility in the process of both Chevron and Amoco [4]. Currently, much efforts are devoted toward the development of more efficient and selective catalysts for oligomerization and polymerization of alkenes by early [5–8] and late transition metal catalysts [9–11]. Ethylene polymerization catalyzed by late transition metal Pd(II) or Ni(II) incorporating α-diimine complexes has been reported by Brookhart et al. [12–15]. Recently, a new family of catalysts based on iron and cobalt complexes containing pyridine bisimine ligands has been found to be very active towards ethylene polymerization when methylaluminoxane (MAO) is used as cocatalyst [16–19]. In their researches on oligomerization of ethylene by Fe(II) and Co(II) complexes, only oligomers with high-average molecular weight were obtained [18].

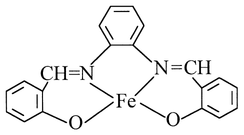
Ethylene oligomerization catalyzed by diimine complexes of late transition metals with ethylaluminoxane (EAO) has not been reported.

---

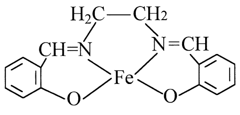
* Corresponding author. Tel.: +86-411-3631333, ext. 3243; fax: +86-411-3633080.

PII: S1381-1169(00)00219-3

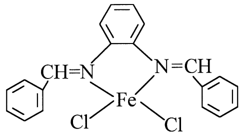
Here we report the ethylene oligomerization catalyzed by a series of iron(II) complexes, Fe(salphen) (**1**) (salphen = N,N'-o-phenylenebis(salicylideneaminato)), Fe(salen) (**2**) (salen = N,N'-ethylenebis(salicylideneaminato)), $FeCl_2$-(PhCH=o-NC_6H_4N=CHPh) (**3**) and $FeCl_2$-(PhCH=NCH_2CH_2N=CHPh) (**4**). The catalytic activities and selectivities of the four complexes with EAO as cocatalyst for ethylene oligomerization have been studied at various reaction temperatures and Al/Fe ratios as well as different reaction periods. The experimental results show that all four complexes have high catalytic activities with satisfying selectivities to low-carbon olefins.



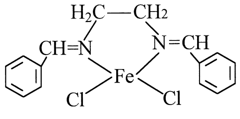
1 Fe(Salphen)



2 Fe(Salen)



3 $FeCl_2$(PhCH=o-NC_6H_4N=CHPh



4 Fe($FeCl_2$(PhCH=NCH_2CH_2N=CHPh)

The structures of the four complexes.

2. Experimental

All reactions were carried out by using standard Schlenk techniques under an atmosphere of nitrogen. Toluene was dried and deoxygenated by distillation also under nitrogen. The other chemicals were purchased commercially and used without further purification.

1, **2**, **3** and **4** were prepared according to the literature [20,21]. EAO was prepared by partial hydrolysis of Et_3Al in toluene at 0–5°C with $Al_2(SO_4)_3 \cdot 18H_2O$ as water source.

The oligomerization reactions were carried out in a 75 ml stainless steel autoclave with magnetic stirring. The autoclave was charged under nitrogen with the solution of catalyst in toluene and 10% EAO toluene solution. Constant temperature was maintained by the electric heating mantle. After the autoclave was pressurized with ethylene to the desired pressure, the reaction mixture was constantly stirred until the end of the reaction. After it has cooled, the vessel was vented and the reaction solution was quenched by adding saturated NaOH–ethanol solution and 1 ml of n-heptane as internal standard. Then, the gas and the solution were analyzed by gas chromatography with an OV 101 column (30 m × 0.25 mm) and FID detector (temperature program: 60–100°C (9°C/min, hold 0 min), 150°C (9°C/min, hold 0 min), 220°C (9°C/min, hold 8 min)). Oligomers were analyzed by HP6890 GC/5973MSD GC-MS detector.

3. Results and discussion

3.1. The effect of reaction temperature on catalytic activities and product distribution

The catalytic activities of catalysts **1**, **2**, **3** and **4** for ethylene oligomerization are strongly affected by reaction temperature (Fig. 1, Table 1). When temperature was raised from 90°C to

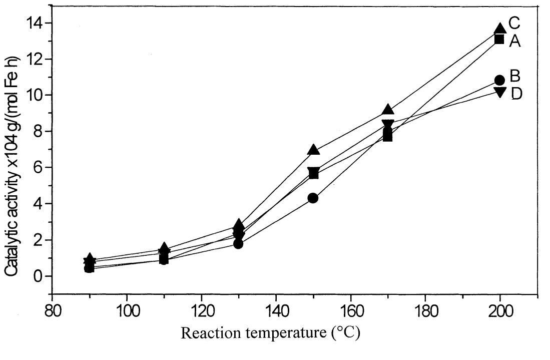


Fig. 1. The effect of temperature on catalytic activity. Reaction conditions: reaction time: 2 h; pressure of ethylene: 1.8 MPa; Al/Fe (molar ratio): 200; iron complex: 0.05 mmol; solvent: toluene; total volume: 30 ml.

Table 1
The effect of reaction temperature on product distribution

Reaction temperature (°C)	Product distribution							
	C_{4-10} olefins				C_{4-10} linear α-olefins			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
90	100	91.2	100	99.4	78.7	95.0	95.9	89.6
110	100	88.6	100	98.8	91.1	78.5	90.6	88.2
130	95.6	83.0	98.2	93.9	78.5	60.7	77.3	75.9
150	87.4	78.3	86.8	83.8	67.9	60.6	65.4	66.3
170	86.1	76.0	83.0	83.7	78.4	67.8	73.6	76.8
200	86.9	73.0	84.8	84.8	58.3	63.0	69.5	66.0

200°C, the activities of the catalysts were greatly increased. In the meantime, the four catalysts displayed a decreased trend of selectivities to C_{4-10} olefins and linear C_{4-10} α-olefins. Such a drastic change of catalytic activities relying on reaction temperature has not been observed in ethylene oligomerization by homogeneous catalysts of early transition metals. This phenomenon might be attributed to the stability of complexes. Complexes **1** and **2** have ligands containing two O,N chelating bonds and large conjugate systems. Complexes **3** and **4** contain N,N′ chelating bonds and large conjugate systems. The catalytic system composed of complex **3**, and EAO is the most active one among the four catalysts. Because complex **3** has a large electron-withdrawing group and the iron–chloride bonds, which are readily alkylated and then undergo chain-growth reaction, high temperature is favorable for the alkylation of iron precatalysts. Compared with Cp_2ZrL_2/EAO (L = Cl, OAr), which was investigated in our previous research [22,23], the catalytic activities of the Fe(II) complexes are much higher at temperatures above 170°C. It seems that iron catalysts are more thermostable than zirconocene catalysts.

3.2. The effect of Al/Fe ratios on catalytic activities and product distribution

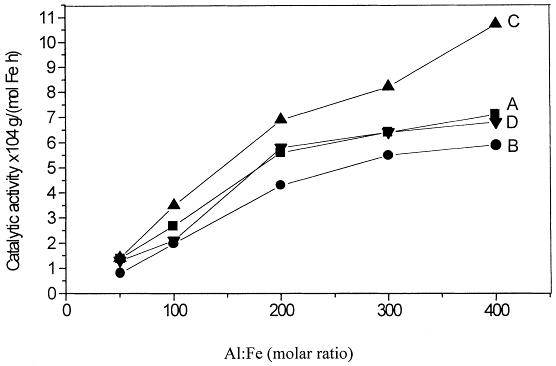


Fig. 2. The effect of Al/Fe ratios on catalytic activity. Reaction conditions: reaction temperature: 150°C. The other conditions are the same as those in Fig. 1.

The effect of Al/Fe ratios on ethylene oligomerization reaction was investigated and the results are shown in Fig. 2 and Table 2. Generally, a threshold amount of cocatalyst was needed to effectively activate the precatalyst. The catalytic activities of the four complexes were enhanced dramatically as the ratio of Al/Fe (mol/mol) was increased from 50 to 200. When the ratio of Al/Fe was higher than 200, the activities went up smoothly, except precatalyst **3**. In addition, the ethylene oligomerization experiment described above showed that the ratio of Al/Fe from 50 to 200 resulted in more active catalysts. These results suggest that catalytically active species formed from precursors containing diimine ligands with steric bulkiness near the metal center could be possibly deactivated through reaction with excess EAO. The catalytic system of complex **3** and EAO performed as the most active one and the activity grew up greatly when Al/Fe ratio was

Table 2
The effect of molar ratios of Al/Fe on product distribution

Al/Fe (molar ratio)	Product distribution							
	C_{4-10} olefins				C_{4-10} linear α-olefins			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
50	93.3	89.3	92.3	90.1	75.5	78.4	75.6	66.6
100	90.0	83.5	89.1	87.3	73.2	69.2	77.4	63.3
200	87.4	78.3	86.8	83.8	67.9	60.6	65.4	66.3
300	90.8	80.3	90.6	86.1	61.0	54.1	70.4	60.6
400	88.7	72.9	89.1	86.7	60.1	56.3	61.7	58.8

above 200. The catalysts kept relatively high selectivities to low-carbon olefins, but the general trend of selectivity of linear C_{4-10} α-olefins was decreased as the ratio of Al/Fe was raised. In general, the structure of alkylaluminoxane has an obvious influence on the catalytic activity and product distribution. Compared with other cocatalysts, like MAO and a modified methylaluminoxane activator (MMAO, in which 25% of the methyl groups have been replaced with isobutyl groups) [12–15], EAO favors the formation of low-carbon olefins for either early or late transition metal precatalysts.

3.3. The effect of reaction time on catalytic activities and product distribution

Catalysts' lifetimes were investigated by measuring the catalytic activities of ethylene oligomerization at different reaction times. The lifetimes of Fe(II) catalysts generated by activation of EAO in ethylene oligomerization are shown in Fig. 3 and Table 3. All used Fe(II) complexes generated the most active catalysts in the first hour. After 3 h, the catalytic activities went down slowly. The catalytic activities of the Fe(II) catalysts in the fourth hour is only about half of that in the first hour. The activities of the four catalysts steadily declined and the selectivities of C_{4-10} olefins and linear C_{4-10} α-olefins gradually decreased with extension time.

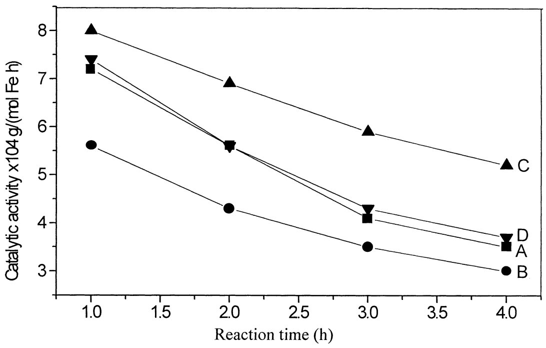


Fig. 3. The effect of reaction time on catalytic activity. Reaction conditions: reaction temperature: 150°C; Al/Fe (molar ratio): 200. The other conditions are the same as those in Fig. 1.

Table 3
The effect of reaction time on product distribution

Reaction time (h)	Product distribution							
	C_{4-10} olefins				C_{4-10} linear α-olefins			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
1	91.1	92.5	98.0	95.8	68.8	70.0	74.4	87.4
2	87.4	78.3	86.8	83.8	67.9	60.6	65.4	66.3
3	89.4	80.5	85.9	77.0	71.5	68.6	73.1	77.4
4	87.0	78.3	87.7	76.4	66.3	66.8	71.7	72.3

4. Conclusion

Four diimine Fe(II) complexes in combination with EAO as cocatalyst displayed high activities in ethylene oligomerization and good selectivities to low-carbon olefins. The catalytic activities of catalysts closely depended on reaction temperature and Al/Fe ratios. The active catalysts reported here are stable over a wide temperature range under a moderate ethylene pressure. The obtained result that the catalytic activity of complex **3** is higher than the activities of complexes **1**, **2** and **4** indicates that two structural factors, iron–chloride bond and large conjugate system, are closely related to the catalytic property of precursors. Therefore, the iron complex with diimine containing the iron–halogen bonds and a large conjugate system is favorable to ethylene oligomerization reactions. Further investigations on other diimine and *N*,*N*,*N*-tridentate-coordinated Fe(II) catalysts for ethylene oligomerization are under way.

Acknowledgements

We gratefully acknowledge the Chinese National Natural Science Foundation (Grant No. 29773008) and the Open Laboratory of Comprehensive Utilization of Carbon Resources, the Chinese Ministry of Education, for financial support of this research.

References

[1] W. Keim, A. Behr, G. Kraus, J. Organomet. Chem. 251 (1983) 377.
[2] W. Keim, R.P. Schulz, J. Mol. Catal. 92 (1994) 21.
[3] M. Peuckert, W. Keim, Organometallics 2 (1983) 594.
[4] D. Vogt, in: B. Cornils, W.A. Hermann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds vol. 1 VCH Publishers, New York, 1996, pp. 245–256.
[5] W. Kamisky, K. Kulper, Angew. Chem., Int. Ed. Engl. 24 (1985) 507.
[6] P.C. Mohring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1.
[7] G.W. Coates, R.M. Waymouth, Science 267 (1995) 217.
[8] X. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10015.
[9] G. Wilke, Angew. Chem., Int. Ed. Engl. 27 (1988) 185.
[10] A. Sen, T.W. Lai, J. Am. Chem. Soc. 103 (1981) 4627.
[11] A.S. Abusurrah, B. Rieger, Angew. Chem., Int. Ed. Engl. 35 (1996) 2475.
[12] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.
[13] C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 11664.
[14] S.A. Svejda, M. Brookhart, Organometallics 18 (1999) 65.
[15] C.M. Killian, L.K. Johnson, M. Brookhart, Organometallics 16 (1997) 2005.
[16] B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143.
[17] B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049.
[18] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Soc., Chem. Commun. 849 (1998).
[19] G.J.P. Britovsek, M. Bruce, C.V. Gibson, J. Am. Chem. Soc. 121 (1999) 8728.
[20] S.C. Marvel, A.S. Aspey, A.E. Dudley, J. Am. Chem. Soc. 78 (1956) 4905.
[21] D.H. Busch, J.C. Bailar, J. Am. Chem. Soc. 78 (1956) 1137.
[22] M. Wang, Y.M. Shen, M.X. Qian, R. He, J. Mol. Catal. (China) 13 (1999) 282.
[23] Y.M. Shen, M. Wang, H. Wang, R. He, Huaxue Tongbao (China) 4 (1999) 32.