

# Ethylene Oligomerization Catalyzed by $MCl_2(PPh_3)_2$ Complexes/Ethylaluminumoxane

QIAN, Ming-Xing(钱明星)    ZHANG, Yu-Liang(张玉良)    HE, Ren\*(何仁)

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, Liaoning 116012, China

The catalytic properties of  $MCl_2(PPh_3)_2$  ( $M = Fe, A; Co, B; Ni, C$ ) in combination with ethylaluminumoxane (EAO) as cocatalyst for ethylene oligomerization have been investigated. Treatment of the  $MCl_2(PPh_3)_2$  complexes with EAO in toluene generated active catalysts *in situ* that are capable of oligomerizing ethylene to low-carbon olefins. The catalytic activity and product distribution were affected by reaction condition, such as reaction temperature, the ratios of Al/M and the reaction time. The activity of  $1.70 \times 10^5$  g oligomers/(mol Co · h) for the catalytic system of  $CoCl_2(PPh_3)_2$  with EAO at 200°C was observed, with the selectivity of 91.1% to  $C_{4-10}$  olefins and 70.7% to  $C_{4-10}$  linear  $\alpha$ -olefins.

**Keywords** Ethylene oligomerization, unidentate phosphine complexes, ethylaluminumoxane

## Introduction

Linear low-carbon  $\alpha$ -olefins are used primarily as comonomers for the production of linear low-density polyethylene, plasticizers and synthetic lubricants. In recent years, the catalytic behavior of late transition metal complexes containing bi- and tri-dentate ligands for oligomerization of ethylene to  $\alpha$ -olefins has been attracting much attention.<sup>1-5</sup> Compared with traditional Ziegler-Natta catalysts of early transition metals, the novel late transition metal catalysts possess advantageous in catalytic activity and selectivity. In their researches on oligomerization of ethylene catalyzed by nickel  $\alpha$ -diimine catalysts and Fe(II), Co(II) bis(imino)pyridine catalysts, the oligomers with high average molecular weight were obtained.<sup>1-4</sup> Ethylene oligomerization catalyzed by iron(II) and cobalt(II) diimine complexes activated by EAO was previously studied in our laborato-

ry.<sup>6,7</sup> However, there is few report referred to the oligomerization of ethylene with unidentate phosphine late transition metal catalysts. Here we report the ethylene oligomerization catalyzed by unidentate phosphine complexes  $FeCl_2(PPh_3)_2$ ,  $CoCl_2(PPh_3)_2$  and  $NiCl_2(PPh_3)_2$  with EAO. The catalytic activities and selectivities of the M(II)-based complexes with EAO as cocatalyst for ethylene oligomerization have been investigated at various reaction temperatures and Al/M ratios, as well as different reaction time. The experimental results show that all these three complexes activated by EAO have moderate catalytic activities for ethylene oligomerization with high selectivities to low-carbon olefins and good selectivities to linear  $\alpha$ -olefins.

## Experimental

### Materials

Toluene was distilled from sodium/benzophenone ketyl prior to use. The other chemicals were purchased commercially and used without further purification.  $FeCl_2(PPh_3)_2$ ,  $CoCl_2(PPh_3)_2$  and  $NiCl_2(PPh_3)_2$  were prepared according to the literature methods.<sup>8-10</sup> 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. Ethylene was purified by passage through a column of molecular sieve (4 Å).

### Oligomerization

*Typical oligomerization procedure* Into a 70 mL

\* Fax: +86-411-3633080; E-mail: ho@mail.dlptt.ln.cn

Received March 13, 2001; revised April 16, 2001; accepted May 14, 2001.

well-dried ampoule, 16.1 mg (0.025 mmol) of  $\text{CoCl}_2\text{-(PPh}_3)_2$  was dissolved in toluene (25 mL), the solution was injected into autoclave, then the toluene solution of EAO (4.8 mL, 5 mmol) was also injected into autoclave under nitrogen atmosphere. The oligomerization reaction was held at 150°C with the pressure of ethylene 1.8 MPa for 2 h. Then, the autoclave was cooled and vented. The reaction mixture was quenched by 2 mL of NaOH ethanol solution and 1 mL of *n*-heptane was added as internal standard. Then the gas and the solution were analyzed by gas chromatography.

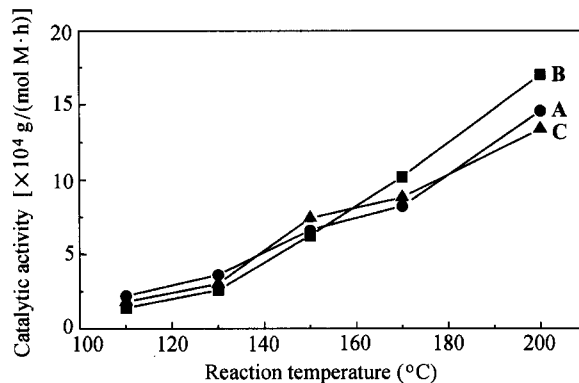
**General oligomerization procedure** The oligomerization reaction was carried out in a 75 mL stainless steel autoclave with magnetic stirring. The autoclave was charged by the solution of unidentate phosphine complexes and 10% EAO toluene solution and then was maintained at constant temperature and ethylene pressure. After the reaction finished, the autoclave was cooled and vented. The reaction mixture was quenched by NaOH ethanol solution and 1 mL of *n*-heptane was added as internal standard. Then the gas and the solution were analyzed by gas chromatography with an OV 101 column (30 m  $\times$  0.25 mm) and flame ionization detector [FID, temperature program: room temperature  $\sim$  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 an HP6890 GC/5973 MSD GC-MS detector.

## Results and discussion

### *Effect of reaction temperature on catalytic activities and product distribution*

A series of experiments were undertaken in order to determine the effect of reaction temperature on catalyst performance. The catalytic activities of catalysts  $\text{FeCl}_2\text{-(PPh}_3)_2$  (A),  $\text{CoCl}_2\text{-(PPh}_3)_2$  (B) and  $\text{NiCl}_2\text{-(PPh}_3)_2$  (C) for ethylene oligomerization are strongly affected by reaction temperature (Fig. 1). When temperature was raised from 110 to 200°C, the activities of the catalysts went up greatly. In the meantime, the three catalysts displayed a decreased trend of selectivities to linear  $\text{C}_{4-10}$   $\alpha$ -olefins (Table 1). The catalytic system composed of complex C and EAO is the most active one at 150°C, but that of complex B and EAO is the most active one at above 150°C and that of complex A and EAO is the most

active one at below 150°C among the three catalysts. Nickel complex had the low catalytic activity at high temperature because parts of nickel complex decomposed probably. The result is in accordance with our former research on iron, cobalt and nickel diimine catalysts with the same ligands. The activity of  $\text{Ni(PhCH = } o\text{-NC}_6\text{H}_4\text{N = CHPh)/EAO}$  [ $14.4 \times 10^4$  g/(mol Ni·h)] is more active than that of  $\text{Fe(PhCH = } o\text{-NC}_6\text{H}_4\text{N = CHPh)/EAO}$  [ $9.1 \times 10^4$  g/(mol Fe·h)] and  $\text{Co(PhCH = } o\text{-NC}_6\text{H}_4\text{N = CHPh)/EAO}$  [ $10.2 \times 10^4$  g/(mol Co·h)] at below 170°C, but the activity of  $\text{Co(PhCH = } o\text{-NC}_6\text{H}_4\text{N = CHPh)/EAO}$  [ $15.0 \times 10^4$  g/(mol Co·h)] is the most active one among the three catalysts at 200°C in our former research.<sup>6,7</sup> This similar result may be caused by the same central metal atom. The activity of  $\text{Co-(PPh}_3)_2\text{/EAO}$  is  $17.0 \times 10^4$  g/(mol Co·h) at 200°C, so the activities of unidentate phosphine complexes are higher than those of diimine complexes. The selectivities of  $\text{C}_{4-10}$  olefins of unidentate phosphine complexes are also higher than those of diimine complexes. Unidentate phosphine complex/EAO catalytic system is excellent for ethylene oligomerization.



**Fig. 1** Effect of temperature on catalytic activity. Reaction conditions: reaction time; 2 h; pressure of ethylene; 1.8 MPa; Al/M (molar ratio); 200; metal complex; 0.025 mmol; solvent; toluene; total volume; 30 mL. A =  $\text{FeCl}_2\text{-(PPh}_3)_2$ ; B =  $\text{CoCl}_2\text{-(PPh}_3)_2$ ; C =  $\text{NiCl}_2\text{-(PPh}_3)_2$ .

### *Effect of Al/M ratios on catalytic activity and product distribution*

In order to explore the role of the cocatalyst in ethylene oligomerization, the ratio of Al/M was varied from 50:1 to 400:1. The results are shown in Fig. 2 and

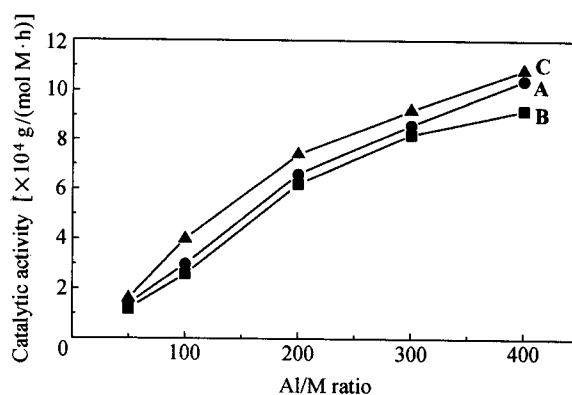
**Table 1** Effect of reaction temperature on product distribution

Reaction temperature (°C)	Product distribution (%)					
	C <sub>4-10</sub> olefins			C <sub>4-10</sub> linear $\alpha$ -olefins		
	A	B	C	A	B	C
110	94.9	92.1	100	91.0	85.4	90.1
130	96.6	94.2	99.3	88.0	83.6	88.2
150	87.0	84.2	88.8	78.4	75.5	78.4
170	89.0	88.5	91.5	78.8	74.5	77.6
200	94.1	91.1	97.9	70.2	70.7	72.9

The reaction conditions are the same as those in Fig. 1.

Table 2. In general, a threshold amount of cocatalyst was needed to effectively activate the catalyst. The catalytic activities of three complexes were enhanced dramatically as the molar ratio of Al/M increased from 50:1 to 200:1. When the ratio of Al/M was higher than 200, the activities went up smoothly. The catalytic system of complex C and EAO performed as the most active one. The selectivities of C<sub>4-10</sub> olefins and linear C<sub>4-10</sub>  $\alpha$ -olefins were obviously decreased when the ratio of Al/M was raised. It is reasonable that the higher ratio of Al/M favors the production of higher molecular weight olefins. The selectivity of C<sub>4-10</sub> olefins and C<sub>4-10</sub> linear  $\alpha$ -olefins catalyzed by unidentate phosphine complexes is higher than that by iron and cobalt diimine complexes.<sup>6,7</sup> From this result, it can be found that the ligands of complexes have obvious effect on catalytic activity

and selectivity to C<sub>4-10</sub> olefins.



**Fig. 2** Effect of Al/M ratios on catalytic activity. Reaction conditions: reaction temperature: 150°C; the other conditions are the same as those in Fig. 1 except for Al/M ratios.

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

Al/M (mol/mol)	Product distribution (%)					
	C <sub>4-10</sub> olefins			C <sub>4-10</sub> linear $\alpha$ -olefins		
	A	B	C	A	B	C
50	95.4	91.2	94.9	88.2	80.4	90.2
100	90.5	88.9	92.0	83.3	77.0	80.6
200	87.0	84.2	88.8	78.4	75.5	78.4
300	86.2	84.0	87.0	71.4	73.2	71.2
400	85.5	81.6	83.6	70.4	66.7	65.4

The reaction conditions are the same as those in Fig. 2.

#### Effect of reaction time on catalytic activity and product distribution

Catalysts were investigated by measuring the catalytic activities of ethylene oligomerization at different reaction time. Activities of unidentate phosphine cata-

lysts generated by activation with EAO in ethylene oligomerization are shown in Fig. 3. Unidentate phosphine complexes needed no aging time to initiate the oligomerization reaction. All M(II) complexes used generated the most active catalysts in the first hour. The activities of three catalysts steadily declined after the first

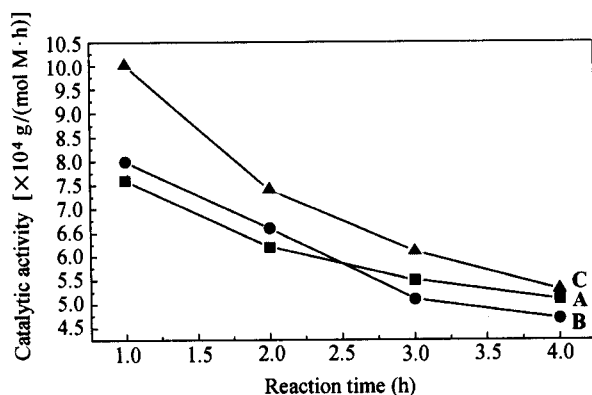
hour and the selectivities of C<sub>4-10</sub> olefins and linear C<sub>4-10</sub> α-olefins gradually decreased with longer time (see Table 3). As the reaction time was prolonged from 1 to 4 h, the proportion of C<sub>4-10</sub> olefins decreased respectively by

11.4% for **A**, 10.7% for **B** and 11.1% for **C**. In order to obtain high selectivity of C<sub>4-10</sub> olefins, an appropriate reaction time should be selected.

**Table 3** Effect of reaction time on product distribution

Reaction temperature (h)	Product distribution (%)					
	C <sub>4-10</sub> olefins			C <sub>4-10</sub> linear α-olefins		
	A	B	C	A	B	C
1	95.4	92.0	98.0	80.1	79.0	79.2
2	87.0	84.2	88.8	78.4	75.5	78.4
3	85.5	81.6	87.9	77.6	75.3	75.2
4	84.0	81.3	86.9	70.6	73.3	75.0

The reaction conditions are the same as those in Fig. 3.



**Fig. 3** Effect of reaction time on catalytic activity. Reaction conditions: reaction temperature: 150°C; the other conditions are the same as those in Fig. 1 except reaction time.

## Conclusion

Unidentate phosphine late transition metal complexes and EAO are novel catalytic system for ethylene oligomerization. Three catalysts displayed moderate activities for ethylene oligomerization and high selectivities to low-carbon olefins. The selectivity of C<sub>4-10</sub> olefins can overcome 91.1% at the optimizing reaction conditions. The activities of catalysts depended greatly on reaction

temperature and Al/M ratios. The complexes **A** and **B** were stable over a wide temperature range under a moderate ethylene pressure.

## References

- 1 Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005.
- 2 Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65.
- 3 Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143.
- 4 Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1998**, 849.
- 5 Beuken, E. K.; Smeets, W. J. J.; Spek, A. L.; Feringa, B. L. *J. Chem. Soc., Chem. Commun.* **1998**, 223.
- 6 Qian, M. X.; Wang, M.; He, R. *J. Mol. Catal. A: Chem.* **2000**, *160*, 243.
- 7 Qian, M. X.; Wang, M.; He, R. *Appl. Catal. A* **2001**, *209*, 11.
- 8 Naldini, L. *Gazz. Chim. Ital.* **1960**, *90*, 391.
- 9 Jensen, L. Z. *Anorg. Chem.* **1936**, *229*, 282.
- 10 Venanzi, L. M. *J. Chem. Soc.* **1958**, 719.