

Ethylene Oligomerization by (dppe)MCl₂ [M = Fe(II), Co(II), Ni(II)] Complexes/EAO

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Abstract: The catalytic properties of a series of (dppe) MCl₂ [M = Fe(II), Co(II), Ni(II)] in combination with EAO (ethylaluminumoxane) for ethylene oligomerization have been investigated. Treatment of the bidentate phosphine metal complexes with EAO in toluene generated *in situ* active catalysts which catalyze oligomerization of ethylene to low-carbon olefins. The effects of reaction temperature, ratios of n(Al) : n(M) and reaction periods on catalytic activity and product distribution have been studied. The activity of cobalt complex with EAO at 200°C was 4021 g/g(Co)·h, and the selectivity of C₄₋₁₀ olefins is 95.5%.

Keywords: Ethylene oligomerization, bidentate phosphine complexes, EAO, α-olefins.

Transition-metal-catalyzed oligomerization of ethylene is an important process to provide α-olefins in the C₆~C₂₀ range. In recent years, the catalytic behavior of late transition metal complexes containing bi- and tri-dentate ligands for oligomerization of ethylene to α-olefins has attracted much attention. When oligomerization of ethylene catalyzed by nickel diimine and Fe(II), Co(II) 2,6-bis(imino)pyridine catalysts, the oligomers with high average molecular weight were obtained¹⁻⁵.

Ethylene oligomerization catalyzed by bidentate phosphine complexes of late transition metals with EAO has not been reported. In this paper we report the ethylene oligomerization catalyzed by a series of bidentate phosphine metal complexes [A = (dppe)FeCl₂; B = (dppe)CoCl₂; C = (dppe)NiCl₂; dppe = 1,2-bis(diphenylphosphine)ethane] with EAO as cocatalyst. The experimental results show that all three complexes activated by EAO have moderate catalytic activities for ethylene oligomerization with high selectivities for low-carbon olefins and good selectivities to linear α-olefins.

Experimental

(dppe) MCl₂[M = Fe(II), Co(II), Ni(II)] were prepared according to the literature methods^{6,7}. EAO was prepared by partial hydrolysis of Et₃Al in toluene at 0 ~ -5°C with Al₂(SO₄)₃·18H₂O as water source. Ethylene was purified by passage through a column of molecular sieve (4 Å). Toluene was distilled over sodium. The other chemicals were purchased commercially and used without further purification.

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The oligomerization reaction was carried out in a 75 mL stainless steel autoclave with magnetic stirring. The autoclave was charged under nitrogen with the solution of bidentate phosphine complexes and 10% EAO toluene solution. Then the reaction mixture was maintained at desired temperature and ethylene pressure. After the reaction finished, the autoclave was cooled and vented. The reaction was quenched by adding saturated NaOH ethanol solution, then 1 mL of *n*-heptane was added as internal standard. The gassy and liquid products were analyzed by gas chromatography with an OV 101 column (30 m×0.25 mm) and FID detector (temperature program: room temperature ~ 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 a HP6890 GC/5973MSD GC-MS detector.

Results and Discussion

The effect of reaction temperature on catalytic activities and product distribution

Table 1 Effect of reaction temperature on catalytic activity and product distribution

T (°C)	Catalytic activity (g/g(M)·h)			Product distribution (%)					
				C ₄₋₁₀ olefins			C ₄₋₁₀ linear α -olefins		
	A	B	C	A	B	C	A	B	C
130	393	746	441	92.6	77.3	97.2	53.0	50.3	89.0
140	636	1356	881	92.2	98.6	98.1	66.4	79.1	88.1
160	1499	2010	1729	92.2	83.9	96.2	77.8	73.2	85.9
180	2785	3018	3356	91.5	89.0	91.1	72.6	70.1	74.2
200	3677	4021	3492	92.6	95.5	93.5	60.9	75.4	68.7

reaction time: 2 h; pressure of ethylene: 1.8 MPa; n(Al) : n(M) = 200; metal complex: 0.025 mmol; solvent: toluene; total volume: 30 mL.

A series of experiments were undertaken in order to determine the effect of reaction temperature on catalyst performance. The catalytic activities of catalysts A, B and C for ethylene oligomerization were strongly affected by reaction temperature. When temperature was raised from 130°C to 200°C, the activities of the three catalysts enhanced obviously, the selectivities to C₄₋₁₀ olefins and linear C₄₋₁₀ α -olefins decreased. The catalytic activity of A was higher than diimine iron(II) complexes/EAO catalysts⁸ for 1000~2000 g/g(Fe)·h. This may be caused by the phosphorus atom's back bonding which made the metal center more electrophilic and the rate of ethylene insertion was increased, the activity-limiting step. Compared with Cp₂ZrL₂ (L = Cl, OAr)/EAO, which was investigated in our previous research⁹, the catalytic activities of the bidentate phosphine complexes were 5-8 times higher than that of zirconocene catalyst at temperature above 170°C. It seems that bidentate phosphine complexes are more thermostable than zirconocene catalysts.

The effect of n(Al) : n(M) ratios on catalytic activity and product distribution

In order to explore the role of the cocatalyst in ethylene oligomerization, the ratios of n(Al) : n(M) from 100:1 to 500:1 have been studied. The results are shown in **Table 2**.

In general, a threshold amount of cocatalyst was needed for activation of the catalyst.

Table 2 Effect of n(Al) : n(M) ratios on catalytic activity and product distribution

n(Al) : n(M)	Catalytic activity (g/g(M)·h)			Product distribution (%)					
				C ₄₋₁₀ olefins			C ₄₋₁₀ linear α -olefins		
	A	B	C	A	B	C	A	B	C
100	1214	1627	1763	97.2	98.7	89.3	73.2	75.7	76.8
200	2785	3018	3356	91.5	89.0	91.1	72.6	70.1	74.2
300	4855	3865	4136	91.2	88.7	91.3	71.4	64.5	70.8
500	5521	5068	5321	89.9	88.4	83.5	60.2	58.2	61.2

reaction temperature: 180°C. The other conditions are the same as those in **Table 1**

The catalytic activities of three complexes were enhanced dramatically as the molar ratio of n(Al) : n(M) increased from 100:1 to 500:1. When n(Al) : n(M) was 100:1, the activity of A was lower than the activities of B and C, while the n(Al) : n(M) ratio reached to 300:1, the activity of A was higher than that of B and C. The selectivities of C₄₋₁₀ olefins and linear C₄₋₁₀ α -olefins were obviously decreased when the ratios of n(Al) : n(M) were raised. So it is necessary to select appropriate ratio of the n(Al) : n(M) in order to obtain high selectivity of C₄₋₁₀ α -olefins. It is reasonable that the high ratio of n(Al) : n(M) favors to the production of higher molecular weight olefins.

The effect of reaction time on catalytic activity and product distribution

Lifetimes of catalysts were investigated by measuring the catalytic activities of ethylene oligomerization at different reaction times. The lifetimes of M(II) bidentate phosphine catalysts in ethylene oligomerization are shown in **Table 3**. The activity of Fe(II)-based bidentate phosphine complex decreased obviously with period of time. The highest activity of three catalysts generated in the first hour and then declined. The selectivities of C₄₋₁₀ olefins and C₄₋₁₀ linear α -olefins gradually decreased with the period of time (see **Table 3**). As the reaction time was prolonged from 0.5 to 3 hours, the proportion of linear C₄₋₁₀ olefins decreased by 13.5% for A, 14.7% for B and 15.8% for C respectively. Branched olefins are increased when reaction time prolonged more than two hours, reincorporation of oligomers was occurred after long reaction periods. In order to obtain high selectivity of C₄₋₁₀ olefins, a shorter reaction time should be selected.

Table 3 Effect of reaction time on catalytic activity and product distribution

Time (h)	Catalytic activity (g/g(M)·h)			Product distribution (%)					
				C ₄₋₁₀ olefins			C ₄₋₁₀ linear α -olefins		
	A	B	C	A	B	C	A	B	C
0.5	3812	3420	3921	93.9	97.0	96.2	78.8	80.1	84.2
1	3524	3220	3824	95.2	95.1	93.2	77.8	71.1	78.2
2	2785	3081	3356	91.5	89.0	91.1	72.6	70.1	74.2
3	2428	2524	2892	82.2	83.9	80.8	66.5	65.4	68.4

reaction temperature: 180°C. The other conditions are the same as in **Table 1**

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