

Ethylene Oligomerization Catalyzed by Nickel(II) Diimine Complexes

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Ethylene oligomerization has been investigated by using catalyst systems composed of nickel(II) diimine complexes (diimine = *N,N'*-*o*-phenylene bis(salicylideneaminato), *N,N'*-*o*-phenylenebisbenzal, *N,N'*-ethylenebisbenzal) and ethylaluminumoxane (EAO). The main products in toluene and at 110—200 °C were olefins with low carbon numbers (C₄—C₁₀). Effects of reaction temperature, Al/Ni molar ratio and reaction period on both the catalytic activity and product distribution were explored. The activity of 1.84 × 10⁵ g of oligomer/(mol_{Ni} · h), with 87.4% of selectivity to C₄—C₁₀ olefins, was attained at 200 °C in the reaction when a catalyst composed of NiCl₂·(PhCH = *o*-NC₆H₄N = CHPh) and EAO was used.

Keywords ethylene oligomerization, nickel complex, diimine ligand

Introduction

Low-carbon linear α -olefins are used primarily as co-monomers for the production of linear low density polyethylene (LLDPE), plasticizers and synthetic lubricants. In recent years, much attention has been attracted to the field of catalytic behavior of late transition metal complexes containing bi- (*N,N*) and tridentate (*N,N,N*) ligands.¹ A new family of catalysts based on iron(II) and cobalt(II) complexes bearing pyridine bisimine ligands was found to be very active towards ethylene polymerization and oligomerization when methylaluminumoxane (MAO) was used as cocatalyst,²⁻⁴ and the nickel(II) and palladium(II) complexes with bulky diimine ligands were reported active for ethylene oligomerization, affording linear α -olefins (C₄—C₂₆).⁵⁻⁷ There is few information about turning the newly found imine complexes of late transition

metals into highly selective catalysts for ethylene oligomerization to low carbon linear α -olefins (C₄—C₁₀).^{8,9} Since an acute shortage of C₆ and C₈ linear α -olefins in our country, in recent years we are interested in the process of ethylene oligomerization by transition metal catalysts.

Iron(II) and cobalt(II) diimine complexes in combination with a cocatalyst of ethylaluminumoxane (EAO) for ethylene oligomerization were previously investigated in our laboratory, which show moderate activities with satisfying selectivity to C₄—C₁₀ olefins.^{10,11} In order to make a systematic comparison, the catalytic properties of analogous Ni(II)-based diimine complexes, Ni(salphen) [**A**, salphen = *N,N'*-*o*-phenylenebis(salicylideneaminato)], NiCl₂(PhCH = *o*-NC₆H₄N = CHPh) (**B**) and NiCl₂(PhCH = NCH₂CH₂N = CHPh) (**C**) (Scheme 1), with EAO as cocatalyst for ethylene oligomerization have been explored at various reaction temperatures and Al/Ni molar ratios, as well as different reaction periods. The experimental results show that the *in-situ* generated Ni(II)-based catalysts activated by EAO have moderate catalytic activities with high selectivity to low-carbon olefins and good selectivity to linear α -olefins.

Experimental

Materials

Toluene was distilled from sodium/benzophenone ketyl prior to use. The other chemicals were purchased

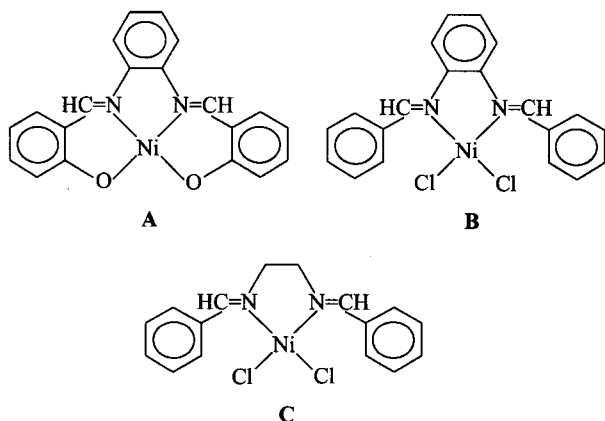
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Received June 18, 2001; revised February 20, 2002; accepted April 16, 2002.

Project supported by the National Natural Science Foundation of China (No. 20173006) and Ph. D.-Starting Fund of Liaoning Province (No. 2001102089).

commercially and used without further purification. Ni(salphen), $\text{NiCl}_2(\text{PhCH} = o\text{-NC}_6\text{H}_4\text{N} = \text{CHPh})$ and $\text{NiCl}_2(\text{PhCH} = \text{NCH}_2\text{CH}_2\text{N} = \text{CHPh})$ were prepared according to the reported methods.^{12,13} EAO was prepared by partial hydrolysis of Et_3Al in toluene at 0 — -5 °C with $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ as water source. Ethylene was purified with molecular sieves (0.4 nm).

Scheme 1



Oligomerization

The oligomerization reactions were carried out in a 75 mL of stainless steel autoclave with magnetic stirring. The autoclave was charged with the solution of the Ni(II) diimine complex and 10 mol% of EAO in toluene, and then was maintained at constant temperature and ethylene pressure during the process. After a given time, the autoclave was cooled and vented. The reaction mixture was quenched by saturated NaOH ethanol solution and 1 mL of *n*-heptane was added as internal standard. The gas and the solution in the autoclave 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 an HP6890GC/5973MSD GC-MS detector.

Results and discussion

Effect of reaction temperature on catalytic activities and product distribution

A series of experiments was undertaken to determine the effect of reaction temperature on catalyst performance.

The results are shown in Table 1. The catalytic activities of catalysts A, B and C for ethylene oligomerization were strongly affected by reaction temperature (Fig. 1). When temperature was raised from 110 °C to 200 °C, the activities of the catalysts were increased obviously. In the meantime, the three Ni(II) catalysts displayed a trend of decreased selectivities to C_4 — C_{10} olefins and C_4 — C_{10} linear

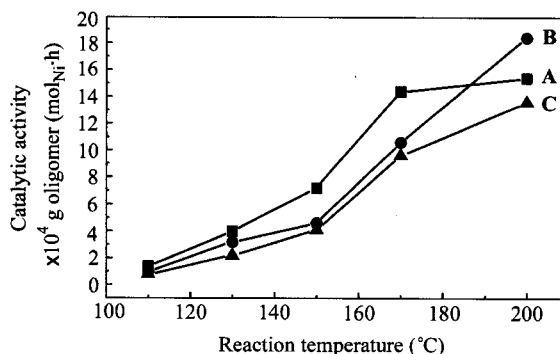


Fig. 1 Effect of temperature on catalytic activity of complexes A, B and C (reaction time: 2 h; pressure of ethylene: 1.8 MPa; Al/Ni (molar ratio): 200; nickel complex: 0.05 mmol; solvent: toluene; total volume: 30 mL). ■—complex A; ●—complex B; ▲—complex C

Table 1 Effect of reaction temperature on product distribution

Reaction temperature (°C)	Product distribution (%) ^a					
	C_4 — C_{10} olefins			C_4 — C_{10} linear α -olefins		
	A	B	C	A	B	C
110	100	100	99.4	90.6	88.2	86.6
130	98.7	96.5	98.1	81.7	78.9	75.4
150	91.3	87.5	90.1	74.2	72.7	71.1
170	93.5	91.1	88.4	70.9	68.4	65.1
200	89.1	87.4	82.7	69.6	63.3	64.3

^a Determined by GC analysis and GC-MS spectra.

α -olefins. The catalytic system composed of complex A and EAO was the most active one below 180 °C, while at 200 °C the system of complex B and EAO was the most active one among the three catalysts. This result is different from that obtained in our previous research with analogous iron(II) catalysts in which the catalyst system of Fe(PhCH = *o*-NC₆H₄N = CHPh)/EAO was more active than that of Fe(salphen)/EAO at the similar reaction temperature.¹⁰ Compared with the systems of other Ni(II) diimine complexes in combination with MMAO (modified methylaluminoxane) as cocatalyst,^{5,6} the selectivity of catalytic

system of **A**, **B** or **C** with EAO towards low carbon α -olefins is apparently improved, but the catalytic activity is an order of magnitude lower than that of the recently reported systems of Ni(II) diimine and bipyridine complexes with MMAO, presumably caused mainly by different cocatalysts.

Effect of Al/Ni molar ratio on catalytic activity and product distribution

In order to explore the role of the cocatalyst in ethylene oligomerization, the molar ratio of Al/Ni was varied from 50:1 to 400:1. The results are shown in Fig. 2 and Table 2. The catalytic activities of the three Ni(II) complexes (**A**, **B** and **C**) were enhanced greatly as the molar

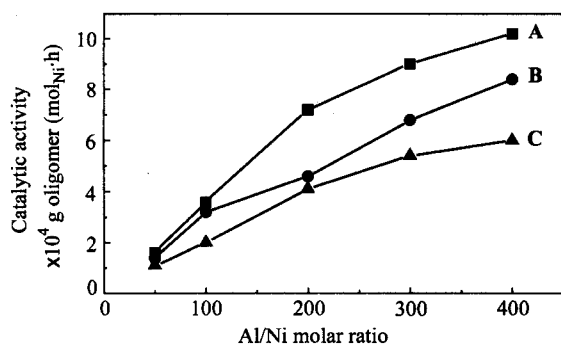


Fig. 2 Effect of Al/Ni molar ratio on catalytic activity (reaction temperature: 150 °C; the other conditions are the same as those in Table 1 except Al/Ni ratio).

Table 2 Effect of molar ratio Al/Ni on product distribution

Al/Ni (mol/mol)	Product distribution (%)					
	C ₄ —C ₁₀ olefins			C ₄ —C ₁₀ linear α -olefins		
	A	B	C	A	B	C
50	100	100	97.4	90.7	89.4	86.8
100	96.9	95.4	94.1	81.6	80.5	79.6
200	91.3	87.5	90.1	74.2	72.7	71.1
300	89.7	86.5	85.7	70.5	68.3	65.9
400	85.6	83.8	81.9	65.3	63.4	61.4

ratio of Al/Ni was increased from 50:1 to 400:1. At the same Al/M molar ratio (Al/M = 200), the activity of Ni(salphen)/EAO was higher than that of Fe(salphen)/EAO [4.4×10^4 g of oligomer/(mol_{Fe}·h)], while the activity of Ni(PhCH = *o*-NC₆H₄N = CHPh)/EAO was lower than that of Fe(PhCH = *o*-NC₆H₄N = CHPh)/EAO

[6.8×10^4 g of oligomer/(mol_{Fe}·h)].¹⁰ The selectivities of C₄—C₁₀ olefins and C₄—C₁₀ linear α -olefins of nickel (II) diimine complexes were somewhat higher than those of analogous iron(II) complexes and decreased as the molar ratio of Al/Ni was raised. It is reasonable that the high molar ratio of Al/Ni favors the production of higher molecular weight olefins.

Effect of reaction time on catalytic activity and product distribution

The correlation of catalytic activity and product distribution of Ni(II) diimine catalysts **A**, **B** and **C** with reaction time was investigated and the results are shown in Fig. 3 and Table 3. No aging time was needed for Ni(II)-based diimine complexes to initiate the oligomerization reaction. All three Ni(II) precursor complexes generated the most active catalysts in the first hour. As

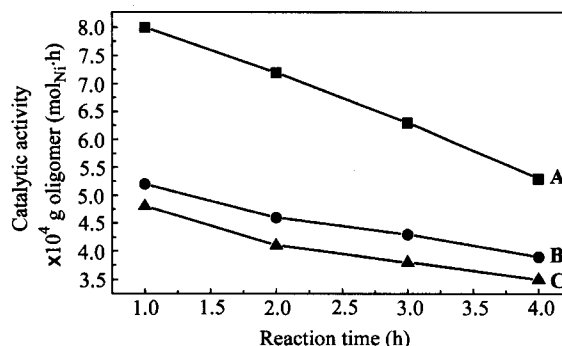


Fig. 3 Effect of reaction time on catalytic activity (reaction temperature: 150 °C; the other conditions are the same as those in Table 1 except reaction time).

Table 3 Effect of reaction time on product distribution

Reaction time (h)	Product distribution (%) ^a					
	C ₄ —C ₁₀ olefins			C ₄ —C ₁₀ linear α -olefins		
	A	B	C	A	B	C
1	98.1	96.8	93.2	81.1	77.4	74.3
2	91.3	87.5	90.1	74.2	72.7	71.1
3	82.4	81.2	80.5	67.3	65.4	64.3
4	72.5	70.4	69.6	62.7	62.3	61.5

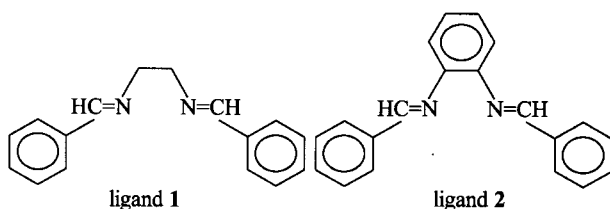
the reaction time extended from 1 h to 4 h, the proportion of C₄—C₁₀ olefins decreased by 24%—26% for precatalysts **A**, **B** and **C**. The decreases in the catalytic activity and the selectivities of C₄—C₁₀ olefins and C₄—C₁₀ linear

α -olefins (Table 3) with reaction time may partially result from the accumulation of low-carbon olefins in toluene with extending reaction time. The dissolved low-carbon olefins can take part in the reaction, leading to higher molecular weight oligomers and branched olefins. In order to obtain high selectivity of C_4 — C_{10} linear α -olefins, a shorter reaction time is required.

Influence of conjugate effect on catalytic activity and product distribution

The results of catalytic reactions by Fe(II)-, Co(II)- and Ni(II)-based catalysts containing either ligand 1 or 2 (Scheme 2) are listed in Table 4 to explore the influence of conjugate effect on catalytic activity and selectivity.

Scheme 2



There are two separate conjugate parts ($-N=CH-Ph$) in the molecule of ligand 1, while the two parts are combined into an integral conjugate system in the mole-

cule of ligand 2 by bonding the two parts to the *ortho*-positions of a benzene ring. For the same center metal ($M = Fe, Co, Ni$), the catalyst with the bidentate coordination of ligand 2 displayed a higher catalytic activity at 200 °C than that with ligand 1. The results in Table 4 show that the catalytic activity of catalysts can be promoted by the coordination of a ligand with a large conjugate system to the center metal of precatalysts. The conjugate extent of a ligand has no obvious influence on the selectivities of low-carbon olefins and linear α -olefins. Under the same reaction conditions and with the same coordination environment, higher selectivities of C_4 — C_{10} linear α -olefins by Co(II)-based diimine catalysts were observed compared with analogous Fe(II)- or Ni(II)-based catalysts.

Conclusion

The catalytic systems composed of Ni(II) diimine complexes **A**, **B** and **C** and EAO displayed moderate activities for ethylene oligomerization and high selectivity to C_4 — C_{10} olefins. The activities of Ni(II) diimine catalysts depended greatly on reaction temperature and Al/Ni molar ratio. The selectivity of 93%—98% to C_4 — C_{10} olefins and 74%—81% to C_4 — C_{10} linear α -olefins were attained at the optimal reaction conditions for **A**, **B** and **C** (1 h, 150 °C, Al/Ni = 200). The Ni(II) diimine catalysts were stable over a wide temperature range under a moderate ethylene pressure.

Table 4 Influence of conjugate effect on catalytic activities and product distribution^a

Center metal	Ligand	Catalytic activity [g/(mol _M ·h), × 10 ⁻⁵]	Product distribution (%)	
			C_4 — C_{10} olefins	C_4 — C_{10} linear α -olefins
Fe ^b	1	1.01	84.8	66.0
	2	1.35	84.8	69.5
Co ^c	1	1.48	84.4	71.2
	2	1.63	85.4	78.6
Ni	1	1.32	82.7	64.3
	2	1.84	87.4	63.3

^a Reaction temperature: 200 °C; the other conditions are the same as those in Table 1. ^b Ref. 15. ^c Ref. 16.

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(E0106184 ZHAO, X. J.; DONG, H. Z.)