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Ethylene Oligomerization to Low Carbon Olefins by a Zirconium Complex Incorporating 8-Quinolinolato Ligands at a Low Al/Zr Ratio

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Abstract: Bis(8-quinolinolato)zirconium dichloride $(Ox)_2ZrCl_2$ (Ox^- = 8-quinolinolato) was found active for ethylene oligomerization with a high selectivity of 84~94% to C_4~C_{10} olefins at 70~100°C under the pressure of 1.8 MPa using Et_2AlCl as a co-catalyst (Al/Zr = 60).

Keywords: Ethylene oligomerization, low carbon olefins, zirconium complex, 8-hydroxyquinoline.

The synthesis and chemistry of early transition metal complexes featuring N,N-, O,O- and N,O-bidentate ligands has gained a lot of attention in virtue of their catalytic applications, especially for olefin polymerization and oligomerization[1]. The continuous increase in the commercial demands for C_4 ~ C_8 linear α-olefins, which are promising as co-monomers of linear low-density polyethylenes (LLDPE), prompts us to focus on the investigation of the high performance homogeneous catalysts for ethylene oligome-rization to low carbon linear α-olefins. Here we report the catalytic property of a zirconium complex incorporating 8-quinolinolato (Ox^-) chelate ligands for ethylene oligomerization in combination with Et_2AlCl as a co-catalyst. Although it has been reported that some titanium and zirconium complexes containing N,O-bidentate ligands are efficient olefin polymerization precatalysts[1,2], the catalytic performance of zirconium complexes having 8-quinolinolato ancillary ligands for ethylene oligomerization is little studied.

Bis(8-quinolinolato)zirconium dichloride $(Ox)_2ZrCl_2$ **1** was prepared from zirco-nium(IV) chloride and 2 equiv of LiOx in diethyl ether according to the literature[3]. The influences of reaction temperature, aging temperature and reaction time on the catalytic activity and product distribution of complex **1** employing Et_2AlCl as a co-catalyst for ethylene oligomerization were studied. The selected results are summarized in **Table 1**. The productivity was calculated to be 108 kg oligomer per mol Zr per h at the optimal conditions (entry 6). The results of entry 1 ~ 4 showed that both catalytic activity and selectivity of complex **1** were affected by the aging temperature. Entry 2 with the aging temperature at 70°C gave the best result of the first 4 entries. Ethylene oligomerization carried out at the aging temperature of 70 ~ 80°C afforded higher selectivity to $C_{4\text{-}10}$ olefins in comparison with the results from entry 1 and 4, while

the selectivity to C_{4-10} linear α-olefins decreased with the increase of aging temperature. When the reaction

Table 1 Selected results of ethylene oligomerization catalyzed by complex **1**[a]

Entry	Temp. °C	Aging temp. °C	Reaction time h	Activity[b] ($\times 10^{-4}$)	C_{4-10} olefins[c] %	C_{4-10} linear α-olefins[c] %
1	90	60	2	5.6	85	88
2	90	70	2	8.2	90	87
3	90	80	2	5.0	93	84
4	90	90	2	4.6	87	74
5	70	70	2	7.0	94	89
6	100	70	2	10.8	84	81
7	110	70	2	7.8	75	78
8	90	70	1	11.2	95	94
9	90	70	3	6.5	85	68
10	90	70	4	5.5	77	64

a) Reaction conditions: zirconium complex 0.025 mmol; cocatalyst Et_2AlCl; Al/Zr(molar ratio) = 60; aging time 0.5 h; $P(C_2H_4)$ = 1.8 MPa; chlorobenzene 30 mL.
b) Activity: g oligomers/mol(Zr)·h.
c) Determined by GC and GC-MS analysis with n-heptane as an internal standard.

temperature was raised from 70 ~ 100°C, the productivity was enhanced apparently (entry 2, 5 and 6), meanwhile, obvious drops in the selectivities to C_{4-10} olefins and to C_{4-10} linear α-olefins were observed for ethylene oligomerization. But further enhancement of reaction temperature resulted in a sharp decrease in the productivity (entry 7). It appears that the active species generated from the system of complex **1**/Et_2AlCl is less thermostable than that from a zirconocene complex/ethylaluminoxane (EAO) where the highest activity was observed at much higher reaction temperature of 150 ~ 200°C in our previous studies[4]. As the reaction time was extended from 1 to 4 hours, the catalytic activity of complex **1** went down from 112 to 55 kg oligomer per mol Zr per h (entry 2 and 8 ~ 10). In the meantime the selectivity decreased from 95 to 77% for C_{4-10} olefins and from 94 to 64% for C_{4-10} linear α-olefins.

In conclusion, bis(8-quinolinolato)zirconium dichloride complex **1** is an effective precatalyst for ethylene oligomerization. The catalytic system of **1**/Et_2AlCl displayed moderate productivity with a high selectivity to low carbon linear olefins.

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