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The effect of cocatalysts on the oligomerization and cyclization of ethylene catalyzed by zirconocene complexes

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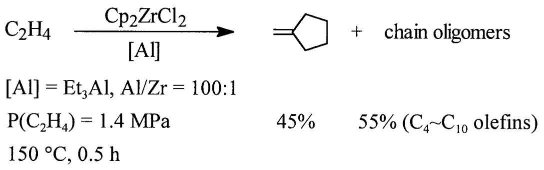
Abstract

Under certain conditions (150°C, $P(C_2H_4) = 1.4$ MPa), the oligomerization of ethylene catalyzed by Cp_2ZrCl_2/EAO (ethylaluminoxane), Et_3Al or $(i\text{-}Bu)_3Al$ afforded methylenecyclopentane (MCP) along with chain oligomers. The nature of cocatalysts and the Al/Zr ratios as well as the hydrolysis extent of Et_3Al have tangible effects on the selectivity of the cyclic oligomer. With Et_3Al as cocatalyst under optimal conditions, the oligomerization of ethylene gave MCP and C_4–C_{10} chain olefins in a ratio of 45/55.



Keywords: Ethylene oligomerization; Cyclization; Zirconocene catalyst; Organo-aluminum compounds; Methylenecyclopentane

1. Introduction

Five-membered carbocyclic compounds are very useful intermediates of some fine chemicals and important feedstock for the production of cycloolefin copolymers. Among the developed methodologies, the most useful tools in organic synthesis are the strategy of $[3+2]$ cyclopentanation [1–3] and the intramolecular couplings of α,ω-diynes, enynes and dienes. These intramolecular cyclizations are either promoted by organometallic compounds of the main group [4] or catalyzed by titanium [5–7], zirconium complexes [8–12] and late-transition-metal compounds [13,14].

In the recent research, we found that under certain conditions, the oligomerization of ethylene catalyzed by Cp_2ZrCl_2/EAO or Et_3Al afforded an unexpected cyclic oligomer, meth-

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ylenecyclopentane (MCP), along with chain oligomers. It is the first example of catalytic formation of a cyclic product direct from ethylene oligomerization. The oligomerization and simultaneous cyclization of ethylene occurring in one pot provides a convenient approach to MCP, in which the *exo*-cyclic methylene group is capable of acting as a very versatile functionality for further elaboration. Here, we report the effect of cocatalysts, including the hydrolysis extent of Et_3Al, the Al/Zr ratios, the nature of aluminum compounds and the reaction time, on the activity and selectivity of the binary catalytic system for the oligomerization and cyclization of ethylene.

2. Experimental

2.1. General methods

All reactions and operations were carried out under a dry, oxygen free dinitrogen atmosphere with standard Schlenk techniques. Ethylene gas was purified by passage through a column of molecular sieve (4 Å). Toluene was distilled from sodium/benzophenone ketyl prior to use.

Zirconium tetrachloride was purchased from Merck-Schuchardt. Other commercially available reagents were used without further purification. Complex Cp_2ZrCl_2 was prepared according to the literature [15]. Triethyl aluminum was carefully distilled in vacuo and cocatalysts EAO (I), (II), (III) and (IV) were prepared, respectively, by partial hydrolysis of Et_3Al at the H_2O/Et_3Al molar ratios of 0.5:1, 1:1, 1.5:1 and 2:1 in toluene at 0–5°C with $Al_2(SO_4)_3 \cdot 18H_2O$ as water source.

2.2. Ethylene oligomerization

Ethylene oligomerization experiment was carried out in a 75 ml stainless steel autoclave with magnetic stirring. The autoclave was dried in vacuo at 200°C for 30 min, cooled to room temperature and filled with pre-purified dinitrogen. A toluene solution of cocatalyst was added to a Schlenk bottle, which was charged with 0.025 or 0.05 mmol of precatalyst Cp_2ZrCl_2 and 15 ml of toluene. All suspended substances were dissolved after stirred for a few minutes. The solution was transferred into the autoclave and the Schlenk bottle was washed with 5 ml of toluene three times. After 30 min of pre-reaction, the autoclave was connected to the line with a continuous constant ethylene pressure (1.4 MPa) and the system was heated to 150°C for a certain period. After reaction, the autoclave was closed, cooled in ice water for 1 h and then vented and weighed. The catalytic activity was calculated from the weight increase of the autoclave after the catalytic reaction. The catalytic system was quenched by addition of 1 ml of NaOH/EtOH saturated solution.

The distribution and the structures of products were determined by GC analysis of the obtained solution with *n*-heptane as internal standard and GC-MS spectra. The cyclic product MCP was isolated by twice careful distillation and detected by ^1H and ^{13}C NMR (JEDLFX-90Q NMR), GC-MS (HP6890GC/5973MS) and GC-IR (HP5890II/Bio-Rad FT S-65A).

3. Results and discussion

The ethylene oligomerization was carried out in anhydrous toluene at 150°C for 2 h under 1.4 MPa of a continuous ethylene pressure by using Cp_2ZrCl_2 as precatalyst (Eq. 1). The catalytic activities and selectivities of Cp_2ZrCl_2/Et_3Al and /EAO (I–IV) are listed in Table 1. The hydrolysis extent of Et_3Al within the given range had no significant influence on the catalytic activity. The results in Table 1 show an obvious tendency that the selectivity of MCP went up as the hydrolysis extent of Et_3Al changes from 2 to 0.5 (H_2O/Et_3Al). The re-

Table 1
Effect of hydrolysis extent of Et_3Al on activities and product distributions[a]

Cocatalyst	TOF[b] ($\times 10^{-3}$)	MCP[c] (%[d])	C_4–C_{10} chain (olefins/%[d])	$\geq C_{12}$ chain (olefins/%[e])
Et_3Al	1.82	39	46	15
EAO (I)	1.96	34	43	23
EAO (II)	2.39	28	35	37
EAO (III)	2.29	26	20	54
EAO (IV)	2.21	11	11	78

[a] Reaction conditions: Zr = 0.025 mmol; Al/Zr = 100; aging temperature: 20°C (30 min); reaction temperature: 150°C (2 h); $P(C_2H_4) = 1.4$ MPa; toluene: 30 ml.

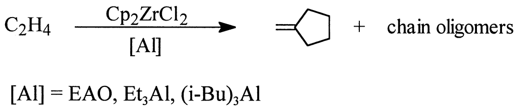
[b] TOF = mol (consumed ethylene)/mol (Zr) h.

[c] MCP = methylenecyclopentane. The product was separated by distillation and identified by GC-MS, GC-IR, ^1H and ^{13}C NMR spectra.

[d] Determined by GC analysis (SE-30, 30 m × 0.25 mm) with internal standard (*n*-heptane).

[e] Calculated by deducting $W(MCP)$ and $W(C_4–C_{10}^{=})$ from the total increasing weight.

placement of EAO with Et_3Al as cocatalyst gave even higher selectivity to MCP (39%). In the meantime, the selectivity of low-carbon chain olefins also increased apparently. The experimental results suggest that the formation of MCP be closely related to the capability of cocatalysts to facilitate the alkylation reaction of precatalyst Cp_2ZrCl_2. We suppose that MCP is formed by a neutral dialkyl zirconocene intermediate $[Cp_2ZrR_2]$ [16], while chain oligomers are generated via a cationic monoalkyl zirconocene $[Cp_2ZrR]^+$, which has been reported as intermediate for the polymerization of ethylene catalyzed by Cp_2ZrCl_2/MAO (methylaluminoxane) [17,18].



(1)

The activities and product distributions resulted from different Al/Zr ratios are summarized in Table 2. Both cocatalysts, Et_3Al and EAO (II), gave the highest selectivities to MCP in the Al/Zr ratio of 100:1. The selectivity of MCP in ethylene oligomerization increased evidently when the ratio of Al/Zr was raised from 25 to 100. Beyond this threshold value, the further enhancement of Al/Zr ratios slightly decreased the selectivity to MCP. In the absence of precatalyst Cp_2ZrCl_2, EAO (II) was capable of oligomerizing ethylene to chain oligomers in a low activity, but no cyclic product MCP was detected by GC analysis.

The nature of aluminum compounds was another important factor affecting the selectivity

Table 2
Effect of the Al/Zr ratios on activities and product distributions[a]

Cocatalyst	Al/Zr (mol/mol)	TOF ($\times 10^{-3}$)	MCP (%)	C_4–C_{10} chain (olefins/%)	$\geq C_{12}$ chain (olefins/%)
Et_3Al	50	1.21	28	53	19
Et_3Al	100	1.82	39	46	15
Et_3Al	120	2.14	36	39	25
Et_3Al	150	1.86	34	34	32
EAO (II)[b]	25	0.5	3	64	33
EAO (II)[b]	50	1.29	10	56	34
EAO (II)[b]	100	1.36	27	34	39
EAO (II)[b]	150	1.36	25	36	39

[a] Except the ratio of Al/Zr, the other reaction conditions are the same as those in Table 1.

[b] $Cp_2ZrCl_2 = 0.05$ mmol.

Table 3
Effect of reaction time on activities and product distributions[a]

Time (h)	TOF ($\times 10^{-3}$)	MCP (%)	C_4–C_{10} chain (olefins/%)	$\geq C_{12}$ chain (olefins/%)
0.5	2.5	45	55	–
1.0	2.04	44	49	7
1.5	1.96	42	39	19
2.0	1.82	39	46	15
2.5	1.64	38	43	19
3.0	1.54	36	40	24

[a] Cocatalyst: Et_3Al. The other conditions are the same as those in Table 1.

of MCP in ethylene oligomerization. When $(i\text{-}Bu)_3Al$ was used as cocatalyst, under identical conditions, the selectivity of MCP went down from 39 for Et_3Al to 30% and the catalytic activity of $Cp_2ZrCl_2/(i\text{-}Bu)_3Al$ system was calculated to be 1.86×10^3 mol (consumed ethylene)/mol (Zr) · h. The higher selectivity to MCP for Et_3Al cocatalyst might be attributed to the ethyl group which is a better β-H donor than the isobutyl group. Presumably, the formation of MCP is proceeded via a zirconacyclopentane intermediate, formed by β-H elemination of Cp_2ZrEt_2 in the presence of ethylene [16]. If cocatalyst Et_3Al was replaced by Et_2AlCl, the oligomerization of ethylene afforded only chain oligomers.

Besides the effect of cocatalysts, we have studied the influence of reaction time on the catalytic activity and selectivity of Cp_2ZrCl_2/Et_3Al for the oligomerization of ethylene. The results showed that MCP was favorably formed in the beginning of catalytic reaction (see Table 3). When the reaction was stopped after half-hour, the selectivities of MCP and C_4–C_{10} chain olefins were 45% and 55%, respectively. Among C_4–C_{10} chain olefins, linear α-olefins accounted for 46% (see Fig. 1). As the reaction time was prolonged, the chemoselectivity to MCP gradually decreased. But even with long reaction time, no *endo*-cyclic olefin, derived from isomerization of *exo*-methylenecyclopentane, was detected in GC analysis. Further investigation is needed to improve the selectivity of MCP and to clarify the mechanism of the novel trimeric cyclization reaction of ethylene.

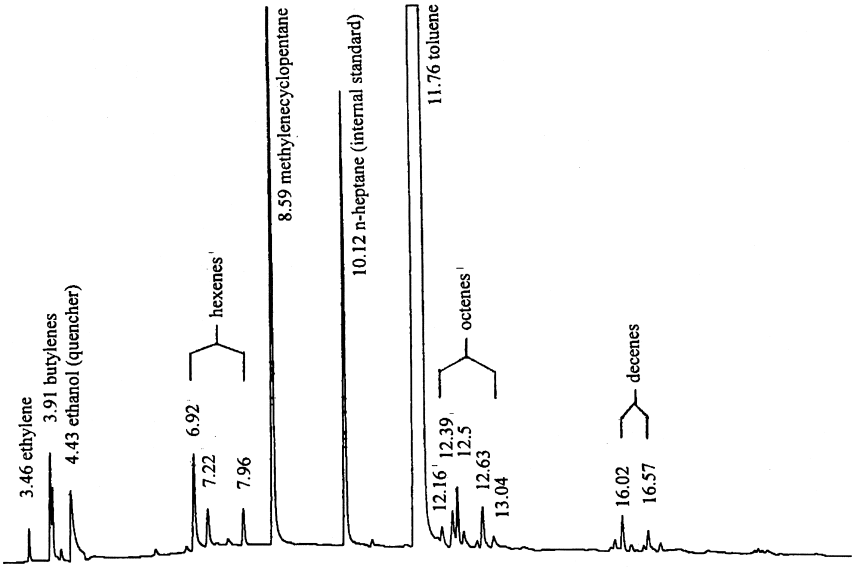


Fig. 1. GC spectrum of the reaction solution. Cocatalyst: Et_3Al. Reaction time: 0.5 h. Other reaction conditions and GC analysis conditions are the same as those given in Table 1.

Acknowledgements

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