

Effects of halide in homogeneous Cr(III)/PNP/MAO catalytic systems for ethylene tetramerization toward 1-octene

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Abstract

In homogeneous Cr(III)/methylaluminoxane/cyclopentyl-bisphosphineamine (PNP)/halide ethylene tetramerization catalyst systems, the effects of halide on the 1-octene formation selectivity and the catalytic activity were investigated. The comparative studies showed that both 1-octene formation selectivity and catalytic activity of the four-member catalytic systems containing dichloromethane were higher than those of containing trichloromethane and tetrachloromethane. 1,1,2-Trichloroethane showed much higher 1-octene formation selectivity improvement than 1,1,1-trichloroethane. The improvement of chloride on 1-octene formation selectivity and catalytic activity was much better than that of a corresponding bromide. So we can draw a conclusion that the steric hindrance, the molecular stability, the halides group configuration, and the types of the halides are important factors for ethylene tetramerization toward 1-octene. Some specific interaction modes of halogen groups with active Cr species in the catalytic cycle are proposed to explain the 1-octene selectivity improvement effects of halide in the ethylene tetramerization reaction. © 2007 Elsevier B.V. All rights reserved.

Keywords: Ethylene tetramerization; 1-Octene; Cr(III) catalyst; Halide

1. Introduction

Trimerization of ethylene to 1-hexene and tetramerization of ethylene to 1-octene have gained increased attention recently due to the importance of 1-hexene and 1-octene in the production of linear low-density polyethylene (LLDPE) [1–3]. Ethylene trimerization and tetramerization route largely avoids the production of undesired olefins that conventional (full-range) olefin oligomerization processes would produce. Over the past few years, 1-hexene and 1-octene market has been expanding at a much faster rate than that of the higher LAOs. Many ethylene trimerization catalyst systems have been developed, and most of them based on chromium catalysts, such as the Phillips–pyrrolide system which was commercialized in Qatar during 2003 [4], the Sasol mixed heteroatomic systems [5,6], and the BP diphosphine system [7]. Tantalum-based system [8] and titanium-based system [9,10] for the selective trimerization of ethylene to 1-hexene have also been reported. The selective tetramerization of ethylene to 1-octene has historically been

considered highly unlikely. However, Annette recently reported a catalyst system [11,12] based on a aluminoxane-activated chromium/ $((R_2)_2P)_2NR_1$ ($R_1 = \text{Me}$, pentyl, cyclohexyl, *i*-propyl and Ph) three-membered systems, capable of giving 1-octene in selectivities of up to 70%.

In our previous research work [13], we found tetrachloroethane can improve the selectivity to 1-octene in Cr(III)/PNP/MAO catalytic system for ethylene tetramerization toward 1-octene. In this article, the effects of various halides on 1-octene formation selectivity in homogeneous Cr(III)/PNP/MAO catalytic systems have been researched in detail. By comparing catalytic activities and selectivities of specific ethylene tetramerization catalyst systems, we also propose plausible chemical interaction modes of halogen groups with Cr catalytic species.

2. Experimental

2.1. Materials

$\text{CrCl}_3(\text{THF})_3$ was purchased from Aldrich and used as received. Methylaluminoxane (MAO, 1.4 mol/L in toluene) was purchased from Albemarle Corp. (USA). All the halides were

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purchased from Beijing Chemical Reagent Co. Ltd. Cyclohexane, toluene, dichloromethane and ethanol were dehydrated and degassed before used. Polymerization grade ethylene was obtained from Daqing Petro-Chemical Ltd. (China). All other chemicals were obtained commercially and used as received.

2.2. Preparation and characterization of PNP ligand

PNP ligand was synthesized according to the method described in literature [12]: To a solution of bis(phenyl) phosphorus chloride (1.33 mL, 7.2 mmol) in dichloromethane (20 mL) and triethylamine (3.75 mL) at 0 °C, cyclopentylamine (0.36 mL, 3.6 mmol) was added. It was stirred for 30 min then the ice bath was removed. After stirring for a total of 14 h the solution was filtered to remove the triethylammonium salt formed. The product was isolated after crystallization in 83% yield. ¹H NMR (δ, ppm, CDCl₃, TMS): 7.24–7.35 (m, 20H, Ar–H), 3.70–3.84 (m, 1H, CH), 1.21–1.85 (m, 8H, CH₂). Anal. calcd. for C₂₉H₂₉NP₂ (453.49): C, 76.81; H, 6.45; N, 3.09. Found: C, 75.69; H, 6.53; N, 3.11%. EI-MS (70 eV): *m/z* = 452.

2.3. Ethylene tetramerization

Ethylene tetramerization was processed in a 500 mL autoclave. After evacuation and flushing with nitrogen three times, then with ethylene two times, the autoclave was charged with 200 mL solvent and magnetically stirred under ambient ethylene atmosphere. When the desired reaction temperature was reached, quantitative MAO, PNP ligand, halide and CrCl₃(THF)₃ were injected into the reactor. Typically 30 min later, the reaction solution was quickly cooled down to 20 °C and then quenched by adding ethanol/HCl (10 wt.%). The catalytic activity was calculated from the increase of product weight.

2.4. Characterization of product

A small sample was washed by deionized water in order to remove alcohol, Cr(III), MAO and chlorohydric acid. The product was dried over anhydrous sodium carbonate and then

analyzed by GC–MS using an HP-5890 with a HP-1 capillary column (30 m × 0.25 mm) and a HP-5971 mass spectroscopy, working at 35 °C (10 min) and then heated at 10 °C/min until reaching 280 °C (remained for 10 min).

3. Results and discussion

In our published results, we found that 1-octene product selectivity has been improved by adding tetrachloroethane to the Cr(III)/PNP/MAO catalytic systems. In order to elucidate the specific effects of the halogen compound on catalytic activity and the selectivity to 1-octene in the Cr(III)/PNP/MAO/halide catalytic systems, different types of halides were applied in the homogeneous ethylene tetramerization catalytic systems. Effects of various halides on catalytic activity and product selectivity of ethylene tetramerization reaction using the standard reaction conditions were compared in Table 1. As shown in Table 1, different types of halides in the Cr(III)/PNP/MAO/halide catalyst systems showed broad ranges of ethylene conversion rates and product selectivities. It can be concluded that all of the seven halides studied can improve 1-octene formation selectivity and the total formation selectivity of 1-hexene and 1-octene under given reaction conditions. The improvement of 1-octene formation selectivity resulted from halides can be explained by the spatial effects of weak coordination of halides on the Cr active species. The catalytic activity decreases significantly with the addition of halides, which may be the effective interaction of halides with Cr centre interfering with the coordination of ethylene and Cr species.

3.1. The comparison of dichloromethane, trichloromethane and tetrachloromethane

In our research, we found that the numbers of halogen atoms connected with specific alkane have important effect on the 1-octene formation selectivity and the catalytic activity. For example, according to the results of dichloromethane, trichloromethane and tetrachloromethane (seen from Table 2), the increase of the halide/Cr molar ratio from 0 to 0.5 increased

Table 1
Effects of halides on catalytic activity and product selectivity

Entry	Halide	Halide/Cr ^a	Activity ^b	Product selectivity wt. %					
				1-C ₄ ⁼	1-C ₆ ⁼	C ₆ H ₁₂ ^c	C ₆ H ₁₀ ^d	1-C ₈ ⁼	1-C ₆ ⁼ + 1-C ₈ ⁼
1	None	0	3.57	0.31	14.16	3.17	3.25	71.74	85.90
2	Dichloromethane	0.5	0.68	0.54	16.35	4.15	3.76	75.20	91.55
3	Trichloromethane	0.5	0.68	1.85	16.05	4.65	4.40	73.59	89.64
4	Tetrachloromethane	0.5	0.48	1.46	16.29	4.58	4.08	73.05	89.34
5	1,1,2-Trichloroethane	0.5	0.30	1.13	15.74	2.69	3.58	74.86	90.60
6	1,1,1-Trichloroethane	0.5	0.77	1.13	15.74	3.88	3.57	74.53	90.27
7	1-Bromobutane	0.5	0.28	1.35	15.31	4.77	3.90	74.30	89.61
8	1-Chlorobutane	0.5	0.25	1.55	15.55	4.71	3.88	74.67	90.22

Reaction conditions: reaction temperature: 55 °C; reaction pressure: 3.0 MPa; reaction time: 30 min; solvent: cyclohexane; Cr(III)/PNP/MAO = 1:2:300 (molar ratio).

^a Molar ratio.

^b 10⁶ g/mol Cr h.

^c Methylcyclopentane.

^d Methylenecyclopentane.

Table 2
Results of ethylene tetramerization with Cr(III)/PNP/MAO/halides

Run	Halide	Halide/Cr ^a	Activity ^b	Product selectivity (wt-%)					
				1-C ₄ ⁼	1-C ₆ ⁼	C ₆ H ₁₂ ^c	C ₆ H ₁₀ ^d	1-C ₈ ⁼	1-C ₆ ⁼ + 1-C ₈ ⁼
1	None	0	3.57	0.31	14.16	3.17	3.25	71.74	85.90
2		0.5	0.68	0.54	16.35	4.15	3.76	75.20	91.55
3		1	0.58	1.64	15.35	4.59	4.17	74.25	89.6
4	Dichloromethane	2	0.48	1.86	14.51	4.92	4.40	74.30	88.81
5		5	0.46	2.51	15.94	4.60	4.05	72.89	88.83
6		10	0.30	1.77	17.07	4.74	3.94	72.48	89.55
7		0.5	0.68	1.85	16.05	4.65	4.40	73.59	89.64
8		1	0.58	1.38	17.95	4.33	4.06	73.76	91.71
9	Trichloromethane	2	0.33	1.46	16.87	4.68	4.08	72.91	89.78
10		5	0.18	1.52	16.90	5.40	4.01	72.16	89.06
11		10	0.09	1.46	16.81	6.57	3.90	71.25	88.06
12		0.5	0.48	1.46	16.29	4.58	4.08	73.05	89.34
13		1	0.37	1.56	15.80	4.74	4.14	72.28	88.08
14	Tetrachloromethane	2	0.10	1.68	16.91	6.31	4.04	71.07	87.98
15		5	0.06	1.78	15.46	7.03	4.11	71.62	87.08
16		10	0.04	2.16	20.43	8.20	3.73	65.48	85.91

Reaction conditions: reaction temperature: 55 °C; reaction pressure: 3.0 MPa; reaction time: 30 min; solvent: cyclohexane; Cr(III)/PNP/MAO = 1:2:300 (molar ratio).

^a Molar ratio.

^b 10⁶ g/mol Cr h.

^c methylcyclopentane.

^d methylenecyclopentane.

the selectivity to 1-octene, whereas with a further increase in the ratio the selectivity to 1-octene declined. It is because the effective interaction of halides with the coordination of ethylene interfering with the coordination of ethylene and Cr species. Both 1-octene formation selectivity and catalytic activity of the catalyst system containing dichloromethane are higher than those containing trichloromethane and tetrachloromethane. This result is opposite to the result of ethylene trimerization catalytic systems reported by Luo et al. [14]. We propose the result is related to the steric hindrance and the molecular stability. The

molecular stability of tetrachloromethane is the biggest, so it is more difficult to coordinate with Cr active species than others.

3.2. The comparison of 1,1,2-trichloroethane and 1,1,1-trichloroethane

One important feature of the halides effect on catalytic activity in the Cr(III)/MAO/PNP/halide catalyst system is observed in the cases of 1,1,2-trichloroethane and 1,1,1-trichloroethane shown in Table 3. 1,1,2-trichloroethane shows much higher

Table 3
Results of ethylene tetramerization with Cr(III)/PNP/MAO/different halides

Run	Halide	Halide/Cr ^a	Activity ^b	Product selectivity (wt.%)					
				1-C ₄ ⁼	1-C ₆ ⁼	C ₆ H ₁₂ ^c	C ₆ H ₁₀ ^d	1-C ₈ ⁼	1-C ₆ ⁼ + 1-C ₈ ⁼
1	None	0	3.57	0.31	14.16	3.17	3.25	71.74	85.90
2		0.5	0.77	1.13	15.74	2.69	3.58	74.86	90.60
3		1	0.35	1.99	14.62	5.29	4.28	73.81	88.43
4	1,1,2-Trichloroethane	2	0.51	2.04	17.76	4.56	3.86	73.55	91.31
5		5	0.64	1.63	17.94	6.10	3.62	73.18	91.12
6		10	0.22	3.84	15.85	6.52	3.72	71.86	87.71
7		0.5	0.30	1.13	15.74	3.88	3.57	74.53	90.27
8		1	0.27	1.16	17.77	3.82	3.69	73.07	90.84
9	1,1,1-Trichloroethane	2	0.22	2.06	15.84	3.99	3.57	71.78	87.62
10		5	0.05	3.22	15.51	2.86	2.69	70.71	86.22
11		10	0.04	5.75	14.90	3.30	2.87	70.07	84.97

Reaction conditions: reaction temperature: 55 °C; reaction pressure: 3.0 MPa; reaction time: 30 min; solvent: cyclohexane; Cr(III)/PNP/MAO = 1:2:300 (molar ratio).

^a Molar ratio.5

^b 10⁶ g/mol Cr h.

^c methylcyclopentane.

^d methylenecyclopentane.

Table 4
Results of ethylene tetramerization with Cr(III)/PNP/MAO/different halides

Run	Halide	Halide/Cr ^a	Activity ^b	Product selectivity (wt.%)					
				1-C ₄ ⁼	1-C ₆ ⁼	C ₆ H ₁₂ ^c	C ₆ H ₁₀ ^d	1-C ₈ ⁼	1-C ₆ ⁼ + 1-C ₈ ⁼
1	None	0	3.57	0.31	14.16	3.17	3.25	71.74	85.90
2		0.5	0.28	1.35	15.31	4.77	3.90	74.30	89.61
3		1	0.15	1.20	18.82	4.98	3.53	71.47	90.29
4	1-Bromobutane	2	0.37	4.89	17.08	4.33	3.52	70.18	87.26
5		5	0.18	3.34	16.82	5.00	3.73	71.11	87.93
6		10	0.12	11.00	15.77	5.50	3.18	64.56	80.33
7		0.5	0.25	1.55	15.55	4.71	3.88	74.67	90.22
8		1	0.14	1.68	16.66	5.27	3.80	72.59	89.25
9	1-Chlorobutane	2	0.90	2.64	17.76	3.85	3.68	72.07	89.83
10		5	0.27	1.34	18.55	4.35	3.71	72.04	90.59
11		10	0.34	4.58	17.06	4.19	3.92	70.25	87.31

Reaction conditions: reaction temperature: 55 °C; reaction pressure: 3.0 MPa; reaction time: 30 min; solvent: cyclohexane; Cr(III)/PNP/MAO = 1:2:300 (molar ratio).

^a Molar ratio.

^b 10⁶ g/mol Cr h.

^c methylcyclopentane.

^d methylenecyclopentane.

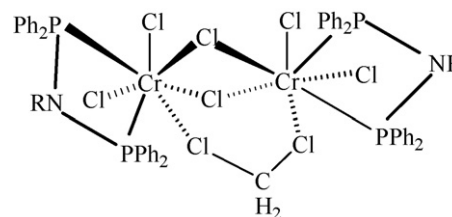
catalytic activity than 1,1,1-trichloroethane, even though the two compounds have the same number of chloro groups and similar properties. The variations in selectivity to 1-octene with the chloro groups configuration means that two chloro groups is enough connect with the same carbon for higher selectivity to 1-octene. The former is better involved in the interaction with other catalytic components for the promotion of catalytic activity. So we propose that the halide groups configuration is very important for the improvement of the catalytic activity and 1-octene formation selectivity.

3.3. The comparison of 1-bromobutane and 1-chlorobutane

From Table 4, it can be concluded the improvement of a chloride on the 1-octene formation selectivity and the catalytic activity is much better than that of a corresponding bromide. Considering that the coordination ability of bromo group with chromium center might be stronger than the coordination ability of chloro group, the catalyst is poisoned slightly comparing with chloride. It might be suggested that the better improvement effect of chloride on both the 1-octene formation selectivity and the catalytic activity is due to a more suitable coordination ability with chromium center.

3.4. Functions of chloro compounds

In order to elucidate the functions of the halide compound in the four-membered catalyst system, we suggest that the effects of halide compound in ethylene tetramerization are arisen by coordination with chromium center to regulate the coordination fashion of chromium species and to make the coordination geometry of chromium center more suitable for ethylene tetramerization. In considering possible cooperative interactions of geminal chloro groups in the catalytic system, we can recall that the catalytic component which interacts with geminal chloro groups requires a specific structural arrange-



Scheme 1. Possible interaction modes between geminal chloro groups and dimeric Cr(III).

ment to fit with and a specific chemical property to interact with catalytic active center. An X-ray structure determination of Cr(III)/PNP complex revealed the chloride-bridged dimer [Cr(PNP)Cl₂(μ-Cl)]₂. The chromium centers of the binuclear complex display a distorted octahedral geometry [12]. The possible coordination structures of halide with chromium center are shown in Scheme 1. In the interaction mode, geminal chloro groups act as two-point weak Lewis base sites which fit with two Cr sites of dimeric Cr(III)/PNP complex. The specific interaction mode between dimeric Cr(III)/PNP complex and geminal chloro groups is expected to stabilize the active center.

4. Conclusions

In the homogeneous chromium(III)/MAO/PNP/halide ethylene tetramerization catalyst system, different halides showed varied effects on the performance of the catalytic system, and suitable halide compound could enhance both 1-octene formation selectivity in ethylene tetramerization. The comparative studies showed that the steric hindrance and molecular stability, the halides group configuration, and the different types of halides were important factors for ethylene tetramerization. Both the 1-octene formation selectivity and the catalytic activity of the catalyst system containing dichloromethane were better than trichloromethane and tetrachloromethane. 1,1,2-trichloroethane showed much higher catalytic activity improvement effect than

1,1,1-trichloroethane. The improvement of a chloride on the 1-octene formation selectivity and the catalytic activity was much better than that of a corresponding bromide. We suggest that the effects of halide compound in ethylene tetramerization are arisen by coordination with chromium center to regulate the coordination fashion of chromium species and to make the coordination geometry of chromium center more suitable for ethylene tetramerization.

References

- [1] U.G. Joung, C.J. Wu, S.H. Lee, et al., *Organometallic* 25 (2006) 5122.
- [2] R. Mülhaupt, *Macromol. Chem. Phys.* 204 (2003) 289.
- [3] K.B. Sinclair, *Macromol. Symp.* 173 (2001) 237.
- [4] Via an internal thermocouple and maintained by cooling Chevron Phillips press release via the web, 21 January 2003, <http://www.cpchem.com>.
- [5] D.S. McGuinness, P. Wasserscheid, W. Keim, et al., *Chem. Commun.* 3 (2003) 334.
- [6] S.M. David, W. Peter, K. Wilhelm, et al., *J. Am. Chem. Soc.* 125 (2003) 5272.
- [7] A. Theodor, J.S. Susan, A.L. Jay, et al., *J. Am. Chem. Soc.* 126 (2004) 1304.
- [8] A. Cecily, B.H. Seth, M. Shahid, et al., *J. Am. Chem. Soc.* 123 (2001) 7423.
- [9] J.M. Theodorus, M. Lionel, R. Pascal, et al., *Organometallics* 22 (2003) 3404.
- [10] H. Bart, *J. Mol. Catal. A: Chem.* 213 (2004) 129.
- [11] B. Annette, B. Kevin, T.D. John, et al., *J. Am. Chem. Soc.* 126 (2004) 14712.
- [12] W. Richard, H.M. David, B. Annette, et al., *Appl. Catal. A: Gen.* 306 (2006) 184.
- [13] T. Jiang, Y.N. Ning, B.J. Zhang, et al., *J. Mol. Catal. A: Chem.* 259 (2006) 161.
- [14] H.K. Luo, D.G. Li, S. Li, *J. Mol. Catal. A: Chem.* 221 (2004) 9.