Preparation of 1-octene by the selective tetramerization of ethylene

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Abstract

A diphosphinoamine ligands has been synthesized. In combination with Cr(III), methylalumoxane (MAO) and tetrachloroethane (TCE), they generate active catalytic systems for ethylene tetramerization toward 1-octene. The effects of reaction temperature, reaction pressure, molar ratio of Al/Cr, TCE/Cr, ligand/Cr, reaction time and sorts of cocatalyst on catalytic activity and selectivity to 1-octene were studied. The results show that the diphosphinoamine/Cr(III)/TCE/MAO four-membered catalytic systems for ethylene tetramerization have improved the selectivity to 1-octene, but catalytic activity is lower than that of three component system. MAO is requisite in forming active species for ethylene tetramerization toward 1-octene. TCE shows significant promotion effect to assist chromium center in improving selectivity toward 1-octene.
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1. Introduction

Linear α-olefins, such as 1-hexene and 1-octene, are used primarily as comonomers for the synthesis of linear low-density polyethylene (LLDPE), plasticizers and synthetic lubricants [1]. The main method of producing 1-hexene and 1-octene is by oligomerization of ethylene. Conventional ethylene oligomerization technologies produce a range of α-olefins following either a Schulz–Flory or Poisson product distribution and specific 1-alkenes are obtained by fractional distillation of the mixture. It limits the content of the 1-octene that can be formed and make a distribution of products. Zahoor et al. [2] synthesized a nickel catalyst used in oligomerization of ethylene to yield a mixture of linear olefins. The selectivity toward linear 1-octene is 19 wt%. The Shell Higher Olefins Process (SHOP) [3] is reported to typically yield 11 wt% 1-octene in its product mixture. Trialkylaluminium catalysts [4] are also commercially used to oligomerize ethylene to mixtures of olefins containing 13–25 wt% 1-octene. Small and Brookhart [5] and Gibson and coworkers [6] have reported highly active ethylene oligomerization catalysts based on iron(II) and cobalt(II) 2,6-bis(imino)pyridyl ligands complexes with methylaluminoxane as cocatalyst. The selectivity of 1-octene is also lower than 20 wt%. Ethylene trimerization has attracted much attention because of their high selectivity to 1-hexene. Many ethylene trimerization catalyst systems have been developed, and most of them based on chromium catalysts, such as the Phillips pyrrolide system [7], the Sasol mixed heteroatomic systems [8,9] and the BP diphosphine system [10]. Tantalum-based system [11] and titanium-based system [12,13] for the selective trimerization of ethylene to 1-hexene have also been reported. However, there is an absence of a commercially successful process for the tetramerization of ethylene to 1-octene selectively.

Recently, Bollmann and coworkers [14–16] have reported an aluminoxane-activated chromium/$((R_2)_2P)_2NR_1$ (R_1 = Me, pentyl, cyclohexyl, *i*-propyl and Ph) three-membered system used in ethylene tetramerization in a good selectivity to 1-octene. On the basis of the previous work of Bollmann, a diphosphinoamine ligand $((Ar_2P)_2NR_1)$ (R_1 = cyclopentyl) (Fig. 1) was synthesized by introducing cyclopentyl substituents on the N atom. Different from Bollmann, we introduced tetrachloroethane as an accelerant in catalytic system for ethylene tetramerization. The effects of reaction temperature, reaction pressure, molar ratio of Al/Cr, TCE/Cr, ligand/Cr, reaction time
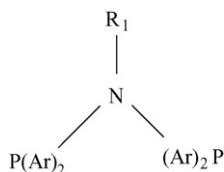

Fig. 1. The structure of diphosphinoamine ligands. R_1 = cyclopentyl; Ar = Ph.

and types of cocatalyst on catalytic properties of four-membered catalytic systems were studied in detail.

2. Experimental

2.1. Materials

Cyclopentylamine and $CrCl_3(THF)_3$ were purchased from Aldrich and used as received. Polymerization grade ethylene was obtained from Daqing Petro-Chemical Ltd. (China). MAO solution (1.4 mol/L) in toluene was purchased from Albemarle Corp. (USA). Cyclohexane, toluene, dichloromethane and ethanol were dehydrated and degassed before used. All other chemicals were obtained commercially and used as received.

2.2. Preparation and characterization of ligand

Ligand was synthesized according to the method described in the literature [14].

To a solution of the 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. ^{1}H NMR (δ, ppm, $CDCl_3$, TMS): 7.24–7.35 (m, 20H, Ar–H), 3.70–3.84 (m, 1H, CH), 1.21–1.85 (m, 8H, CH_2). Anal. calcd. for $C_{29}H_{29}NP_2$ (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 ethy-
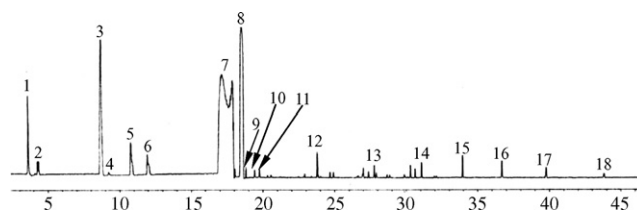

Fig. 2. The chromatogram of ethylene tetramerization products: (1) ethylene, (2) 1-butylene, (3) 1-hexene, (4) n-hexane, (5) methyl cyclopentane, (6) methylene cyclopentane, (7) toluene (reaction solvent), (8) 1-octene, (9) 1-octane, (10) octadiene, (11) 2-octene, (12) 1-decene, (13) 1-dodecene, (14) 1-tetradecene, (15) 1-hexadecene, (17) 1-octadecene and (18) C20 1-alkene.

lene atmosphere. When the desired reaction temperature was established, quantitative MAO, ligand and $CrCl_3(THF)_3$ 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 is 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, 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), the results are shown in Fig. 2.

3. Results and discussion

The four-membered active catalyst was produced in situ by introducing a mixture of $CrCl_3(THF)_3$, tetrachloroethane and the ligand to an autoclave containing solvent and MAO.

3.1. The effect of reaction temperature on catalytic properties

The catalytic activities and selectivity to 1-octene of four-membered catalytic systems for ethylene tetramerization are strongly affected by reaction temperature, as shown in Table 1. The catalytic activity increases initially with temperature and reaches a maximum around 50 °C. As reaction temperature increases from 50 to 80 °C, the activities of the catalysts decrease significantly. There are two counter-effects to this that likely

Table 1
Effects of reaction temperature on catalytic activity and product selectivity

Temperature (°C)	Activity (10^6 g/mol cat. h)	Product selectivity (%)									
		1-$C_4^=$	1-$C_6^=$	1-$C_8^=$	1-$C_{10}^=$	1-$C_{12}^=$	1-$C_{14}^=$	1-$C_{16}^=$	1-$C_{18}^=$	1-$C_{20}^=$	>1-$C_{22}^=$
40	11.60	0.15	9.38	72.60	1.11	0.39	0.44	0.51	0.38	0.24	0.24
50	11.90	0.47	10.76	72.70	1.13	0.41	0.46	0.56	0.41	0.22	0.16
60	7.57	0.43	13.86	70.44	1.13	0.41	0.42	0.48	0.35	0.25	0.41
70	6.53	0.50	14.55	69.30	1.37	0.75	0.56	0.79	0.48	0.30	0.43
80	6.23	0.56	17.32	64.48	1.88	1.00	1.09	0.96	0.78	0.58	0.82

Reaction conditions—solvent: cyclohexane; reaction pressure: 5.0 MPa; Cr(III):ligand:MAO:TCE = 1:2:300:1; reaction time: 30 min.

Table 2
Effects of reaction pressure on catalytic activity and product selectivity

Pressure (MPa)	Activity (10^6 g/mol cat. h)	Product selectivity (%)								
		1-$C_6^=$	1-$C_8^=$	1-$C_{10}^=$	1-$C_{12}^=$	1-$C_{14}^=$	1-$C_{16}^=$	1-$C_{18}^=$	1-$C_{20}^=$	>1-$C_{22}^=$
1.0	2.00	33.51	54.43	0.81	0.17	0.11	0.09	0.06	0.05	0.03
2.0	3.54	22.94	60.67	1.03	0.28	0.24	0.25	0.2	0.13	0.15
3.0	9.14	18.95	64.25	1.17	0.35	0.34	0.40	0.33	0.24	0.37
4.0	10.64	16.83	68.53	1.32	0.48	0.46	0.49	0.37	0.25	0.41
5.0	12.70	15.06	72.70	1.38	0.53	0.49	0.53	0.42	0.35	0.62
6.0	16.08	14.76	73.10	1.45	0.56	0.54	0.69	0.59	0.48	0.88

Reaction conditions—solvent: cyclohexane; reaction temperature: 50°C; Cr(III):ligand:MAO:TCE = 1:2:300:1; reaction time: 30 min.

Table 3
Effects of Al/Cr molar ratios on catalytic activity and product selectivity

Al/Cr (mol/mol)	Activity (10^6 g/mol cat. h)	Product selectivity (%)									
		1-$C_4^=$	1-$C_6^=$	1-$C_8^=$	1-$C_{10}^=$	1-$C_{12}^=$	1-$C_{14}^=$	1-$C_{16}^=$	1-$C_{18}^=$	1-$C_{20}^=$	>1-$C_{22}^=$
75	10.46	0.51	12.29	69.46	1.03	0.41	0.47	0.64	0.57	0.46	0.74
200	10.42	0.54	12.15	71.70	0.91	0.26	0.24	0.35	0.22	0.00	0.00
250	10.72	0.24	13.69	71.85	0.95	0.31	0.36	0.45	0.31	0.19	0.25
300	12.70	0.01	16.75	72.70	0.92	0.29	0.35	0.44	0.32	0.16	0.10
350	12.44	0.31	14.16	71.10	0.96	0.21	0.34	0.43	0.35	0.26	0.33
400	10.38	0.60	15.60	69.35	0.87	0.27	0.33	0.38	0.25	0.12	0.10

Reaction conditions—solvent: cyclohexane; reaction temperature: 50 °C; reaction pressure: 5.0 MPa; Cr(III):ligand:TCE = 1:2:1; reaction time: 30 min.

exist. Firstly, elevated temperatures are expected to result in overall higher propagation and transfer rates and therefore higher productivities. Secondly, higher temperatures can result in lower ethylene solubility and higher rates of catalyst deactivation, which can lead to reducing productivity [17]. It is a combination of these effects that is likely to account for the observed temperature dependence of the productivity. The selectivity to 1-octene displays a decreasing trend with the increase of reaction temperature. It indicates that the rate of chain transfer increases more than the rate of propagation, which is expected to afford lower molecular weight products [18].

3.2. The effect of reaction pressure on catalytic properties

The effect of reaction pressure on catalytic properties is shown in Table 2. Improving ethylene pressure dramatically

increased catalytic activity and selectivity to 1-octene. The selectivity to 1-hexene decreased and higher oligomers increased. This result shows that the elevated pressure led to an increase of ethylene concentration in solvent [11], which results in the increase of chain propagation rate and thus induce the increase of catalytic activity and selectivity to 1-$C_8^=$.

3.3. The effect of Al/Cr molar ratios on catalytic properties

The effect of Al/Cr molar ratios on catalytic properties is investigated and the results are shown in Table 3. The catalytic activity went up obviously as the molar ratio of Al/Cr was increased from 50 to 300. When the molar ratio of Al/Cr was further increased, the catalytic activity decreased. The selectivity to 1-octene as the molar ratio of Al/Cr was enhanced reaches a maximum around 300. With the increases

Table 4
Effects of TCE/Cr molar ratios on catalytic activity and product selectivity

TCE/Cr (mol/mol)	Activity (10^6 g/mol cat. h)	Product selectivity (%)									
		1-$C_4^=$	1-$C_6^=$	1-$C_8^=$	1-$C_{10}^=$	1-$C_{12}^=$	1-$C_{14}^=$	1-$C_{16}^=$	1-$C_{18}^=$	1-$C_{20}^=$	>1-$C_{22}^=$
0	18.76	0.43	12.12	71.83	1.04	0.34	0.38	0.59	0.37	0.22	0.29
0.8	15.22	0.21	11.64	72.35	1.09	0.39	0.45	0.61	0.49	0.36	0.53
1.6	9.14	0.31	14.16	72.49	0.96	0.21	0.34	0.43	0.35	0.26	0.33
2.4	7.92	0.40	13.01	72.74	1.00	0.34	0.38	0.48	0.36	0.27	0.44
3.6	7.28	0.32	12.52	72.91	0.97	0.34	0.42	0.54	0.50	0.42	0.52
4.8	6.46	0.40	11.53	73.21	1.07	0.26	0.49	0.66	0.49	0.29	0.24
6	4.86	0.37	12.22	73.57	0.97	0.31	0.37	0.61	0.47	0.33	0.42
7	4.46	0.44	11.42	74.34	0.98	0.32	0.38	0.48	0.35	0.24	0.21
8	3.58	0.39	11.89	74.67	1.00	0.33	0.38	0.50	0.40	0.31	0.48
10	3.42	0.32	12.35	74.94	0.96	0.32	0.36	0.47	0.35	0.24	0.33

Reaction conditions—solvent: cyclohexane; reaction temperature: 50 °C; reaction pressure: 5.0 MPa; Cr(III):ligand:MAO = 1:2:300; reaction time: 30 min.

Table 5
Effects of ligand/Cr molar ratios on catalytic activity and product selectivity

Ligand/Cr (mol/mol)	Activity (10^6 g/mol cat. h)	Product selectivity (%)									
		$1\text{-}C_4^=$	$1\text{-}C_6^=$	$1\text{-}C_8^=$	$1\text{-}C_{10}^=$	$1\text{-}C_{12}^=$	$1\text{-}C_{14}^=$	$1\text{-}C_{16}^=$	$1\text{-}C_{18}^=$	$1\text{-}C_{20}^=$	$>1\text{-}C_{22}^=$
1.0	15.58	1.38	14.22	69.34	1.11	0.39	0.40	0.44	0.36	0.28	0.47
1.2	10.54	0.44	14.64	69.62	1.06	0.39	0.47	0.60	0.53	0.41	0.51
1.4	8.12	0.38	13.36	70.61	1.11	0.42	0.50	0.62	0.48	0.39	0.70
1.6	7.52	0.41	15.45	70.31	0.98	0.34	0.38	0.48	0.35	0.25	0.39
1.8	7.30	0.39	13.93	71.52	1.00	0.34	0.39	0.44	0.30	0.18	0.16
2.0	7.14	0.31	14.16	71.74	0.96	0.21	0.34	0.43	0.35	0.26	0.33
4.0	1.324	0.44	11.76	70.20	1.00	0.36	0.51	0.84	0.78	0.63	1.03

Reaction conditions—solvent: cyclohexane; reaction temperature: 50 °C; reaction pressure: 5.0 MPa; Cr(III):MAO:TCE = 1:300:1; reaction time: 30 min.

of Al/Cr molar ratio from 300 to 400, the catalytic system displays a decreasing trend of selectivity to 1-octene [19]. It also appears that more 1-hexene is made. Similar results have been reported by Yang et al. [20] in [Cr(2-ethylhexanoate)₃/2,5-dimethylpyrrole/triethylaluminum/chloro compound] catalyst system for ethylene trimerization. This is expected that any excess amount of alkylaluminium or alkylalumoxane may interfere with the formation of active Cr species and/or by the over-reduction of Cr species.

3.4. The effect of TCE/Cr molar ratios on catalytic properties

For homogeneous chromium-based four-membered catalyst system [Cr(III)/ligand/MAO/TCE], the TCE/Cr molar ratio has significant effects on both selectivity to 1-octene and catalytic activity. The results of studies on TCE/Cr molar ratio from 0 to 10 are listed in Table 4. It shows the effect of TCE/Cr molar ratio on catalytic activity, with the increasing of TCE/Cr molar ratio the catalytic activity decreases quickly. With the increasing of TCE/Cr molar ratio from 0 to 10, the selectivity to 1-octene is increased. The 1-octene product selectivity improvement effect of chloro compound can be explained by the spatial effects of weak coordinations of chloro groups on the Cr active species, which modify spatial and electronic properties of active sites. It prevents the coordination of ethylene with chromium center and β-H transferring from chromacycloheptane resulting in lower catalytic activity and higher selectivity to 1-octene [20,21].

3.5. The effect of ligand/Cr molar ratios on catalytic properties

The ligand/Cr molar ratio also has significant effects on catalytic activity and selectivity to 1-octene in chromium-catalyzed ethylene tetramerization four-membered catalytic systems. The results are shown in Table 5. It shows clearly that, increasing ligand/Cr molar ratio from 1 to 4 resulted in an evident decrease of catalytic activity. When ligand/Cr molar ratio is 2 the selectivity to 1-octene reaches the highest values. It indicates that the formation of active Cr species is related to the interactions of other catalytic components of proper ratios. The excess amount of ligand component may interfere with the formation of active Cr catalytic species [20,21].

3.6. The effect of reaction time on catalytic properties

Catalyst lifetimes were investigated by measuring the ethylene flow into the reactor with a mass flowmeter. The effect of
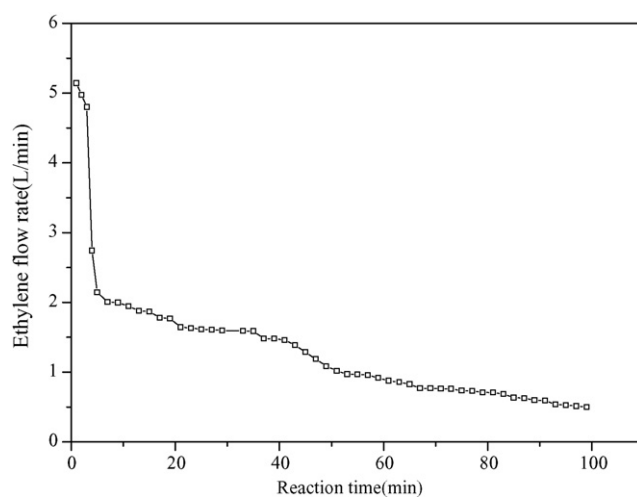

Fig. 3. Effect of reaction time on catalytic activity. Reaction conditions—solvent: cyclohexane; reaction temperature: 50 °C; reaction pressure: 5.0 MPa; Cr(III):ligand:MAO:TCE = 1:2:300:1.
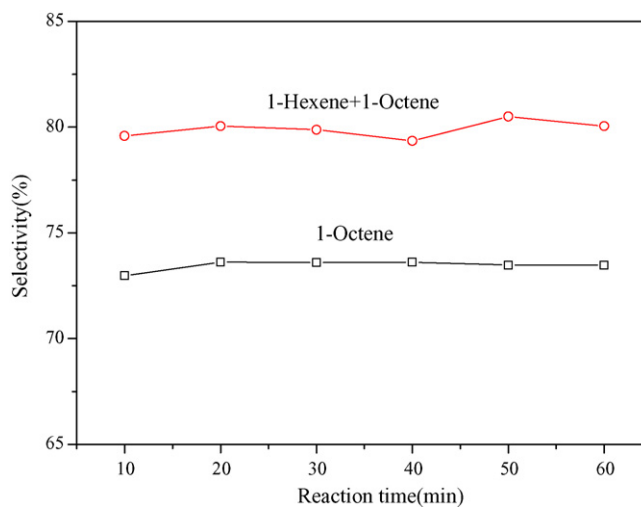

Fig. 4. Effect of reaction time on selectivity. Reaction conditions—solvent: cyclohexane; reaction temperature: 50 °C; reaction pressure: 5.0 MPa; Cr(III):ligand:MAO:TCE = 1:2:300:1.

Table 6
Effect of sorts of cocatalyst on catalytic properties

Entry	Cocatalyst	Activity (10^6 g/mol cat. h)	1-Octene (%)	1-Hexene (%)	1-Butene (%)
1	EAO	3.22	40.07	42.42	3.93
2	TEA	2.01	17.19	24.02	37.19
3[a]	TEA	1.70	1.52	95.39	0.48
4	MAO	18.78	71.89	12.17	1.23

Reaction conditions—solvent: cyclohexane; reaction temperature: 50 °C; reaction pressure: 5.0 MPa; Cr(III):ligand = 1:2; reaction time: 30 min. Al/Cr = 300.

[a] TCE has been add and TCE/Cr = 1.

catalyst lifetimes on catalytic activity and selectivity to 1-octene are shown in Figs. 3 and 4. The high ethylene flow rates during the initial 5 min reaction reflect the process of ethylene saturation in the solvent. It indicates that the catalytic activity is stable over 40 min reaction periods. After this time catalyst activity steadily declines. The selectivity to 1-octene is invariable over reaction periods. Catalyst inactiveness should be responsible for the decrease of catalytic activity.

3.7. The effect of cocatalysts on catalytic properties

Three kinds of alkylaluminium were used as cocatalyst in ethylene tetramerization. The effects of alkylaluminium species on catalytic activity and selectivity to 1-octene are shown in Table 6. The order of catalytic activity and selectivity to 1-octene are: MAO > EAO > TEA. It indicates that MAO is requisite in forming active species for ethylene tetramerization toward 1-octene with highly selectivity. Methylaluminoxane (MAO) is a powerful activator for metallocenes and late-transition metal complexes in the field of olefin polymerization catalysis. Despite intense interest from both academic and industrial laboratories, the structure and function of MAO is not well understood [22]. The important chemical functions of MAO in catalytic systems can also be counted in the selectivity toward 1-octene and catalytic activity. It is notable that when adding TCE to Cr(III)/ligand/TEA catalytic system, the selectivity to 1-hexene is up to 95.39%. It tells us TCE play an important role in catalytic systems for ethylene tetramerization. The research on effect of cocatalyst on catalytic properties, such as tri-isobutylaluminum, AlEt$_2$Cl, EAO, TMA and MAO without TMA is underway. The role of cocatalyst on catalytic properties will be reported in detail in the near future.

4. Conclusions

Four-membered catalytic systems display high activities in ethylene tetramerization with good selectivities to 1-octene. The catalytic activities and selectivity to 1-octene closely depend on types of cocatalyst and reaction conditions. TCE can improve the selectivity to 1-octene but decreases the catalytic activity. Further research on the mechanism of TCE, on the mechanism of cocatalyst and novel accelerant are ongoing.

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