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Preparation of 1-octene by ethylene tetramerization with high selectivity

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Abstract Two novel PNP ligands have been synthesized and characterized by ^{1}H-NMR, elemental analysis, and mass spectra. In combination with Cr(Ⅲ) and cocatalyst MAO, they generate active catalytic systems that tetramerize ethylene with both high catalytic activity and high selectivity to produce 1-octene. The results show that these catalyst systems are able to catalyze ethylene tetramerization, with high catalytic activity up to 0.89×10^6 g/mol Cr.h, and the selectivity of C_8 in products is 72.52%, and the percentage of 1-olefins in the C_8 cut is 97.87%.

Keywords: ethylene tetramerization, 1-octene, Cr(Ⅲ), MAO.

1-Octene is widely used in the chemical industry as a comonomer for linear low-density polyethylene (LLDPE), plasticizers, detergent alcohols and synthetic lubricants[1]. The ethylene copolymer with 1-octene as comonomer has better mechanical properties, optics properties, tear and impact resistance than those with 1-butene or 1-hexene as comonomer[2]. There is no commercially successful process for tetramerizing ethylene to 1-octene selectively. Usually, 1-octene is prepared by ethylene oligomerization or extraction process in industry. Except for chromirum catalyst used in ethylene trimerization, other ethylene oligomerization catalysts produce a range of α-olefins following either a Schulz-Flory or Poisson product distribution. The selectivity of 1-octene is about 10%—20% in the mixture of products[2—4].

Recently, Annette *et al.*[5—7] has reported an aluminoxane-activated chromium/$(Ar_2P)_2NR_1$(R_1=Me, Pentyl, Cyclohexyl, *i*-Propyl and Ph) system used in ethylene tetramerization with a good selectivity for 1-octene. It breaks through the common belief that ethylene tetramerization toward 1-octene is improbable via a nine-membered metallacycle intermediate[8—10]. In this paper, two bridged diphoshinoamine ligands $(((Ar_2P)_2N)_2R)$ ($R=C_2H_4$(**1**) and $R=C_6H_{12}$(**2**)) (Fig. 1) are synthesized and characterized. With MAO as co-catalsyt, the effects of reaction conditions on the properties of Cr(Ⅲ)/PNP(1,2)/MAO systems for ethylene tetramerization to produce 1-octene have been investigated.

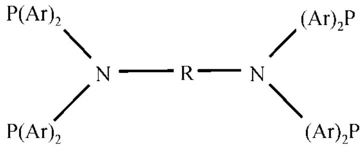

Fig. 1. Bridged diphoshinoamine ligands **1**, $R=C_2H_4$; **2**, $R=C_6H_{12}$.

1 Experiment

1.1 *Materials*

Bis(phenyl)phosphorus chloride, $CrCl_3(THF)_3$ were purchased from Aldrich and used as received. Polymerization grade ethylene and high pure nitrogen were obtained from Daqing Petro-Chemical Ltd. (China). MAO solution (1.4 mol/L) in toluene was purchased from Albemarle Corp. (USA). Toluene, dichloromethane, triethylamine, ethanediamine, 1,6-hexamethylendiamine were obtained commercially and used after dehydration through 4A molecular sieve.

1.2 *Preparation and characterization of ligands*

Ligands **1** and **2** were synthesized according to the method described in ref. [5]:

Ligand of **1**($C_{50}H_{44}N_2P_4$) ^{1}H NMR($CDCl_3$): δ= 7.29—7.17 (t, Ar-H), 3.18 (d, CH_2). Elemental analysis: Calc.(%): C 75.37, H 5.57, N 3.52; Found (%): C 74.92, H 5.38, N 3.58. EI-MS (70 eV): *m/z*=796.

Ligand of **2**($C_{54}H_{52}N_2P_4$) ^{1}H NMR($CDCl_3$): δ= 7.36—7.26（t, Ar-H）, 3.14—3.02 (t, CH_2), 0.89 (m, CH_2), 0.56 (m, CH_2). Elemental analysis: Calc. (%): C 76.04, H 6.15, N 3.28. Found (%): C 75.89, H 6.28, N 3.19. EI-MS (70 eV): *m/z* = 853.

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

1.3 *Ethylene tetramerization*

Ethylene tetramerization was processed in a 500 mL autoclave. After evacuation and flushing with nitrogen three times, and then with ethylene twice, the autoclave was charged with 200 mL solvent and magnetically stirred under ambient ethylene 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℃ and then quenched by adding HCl/ethanol (10 wt%). The catalytic activities were computed by increase of the product.

1.4 Characterization of product

Solid products were isolated from the reaction mixture by filtration, dried overnight in an oven at 100℃ and then weighed. A small sample of the filtrate was washed by water in order to remove alcohol, MAO and chlorohydric acid. The product was dried over anhydrous sodium carbonate and then analysed by GC-MS using an HP-5890 with an HP-1 capillary column (30 m×0.25 mm) and an HP-5971 mass spectroscopy, working at 35℃(10 min) and then heated at 10℃/min until 220℃ (remained for 10 min), and the results are shown in Fig. 2.

2 Results and discussion

2.1 The effect of ligand structure on catalytic properties

The effect of ligand structure on catalytic properties is shown in Table 1. The results in Table 1 indicate that both catalysts **1** and **2** can also catalyze ethylene tetramerization to produce 1-octene with high selectivity under appropriate condition. Under the same condition, catalyst **2** has higher catalytic activity toward ethylene tetramerization than catalyst **1**, because the longer hexyl bridge in ligand **2**, comparing with ethyl bridge in ligand **1**, induces two nuclei far from each other and thus benefits the insertion of ethylene resulting in higher catalytic activity. Catalyst **2** has high selectivity of $1\text{-}C_6^=$ and $1\text{-}C_8^=$, which suggests that the ligand structure has important effect on catalytic properties.

Table 1 The effect of ligand structure on catalytic activity and product selectivity

Ligand	Activity $^{a)}$	C_6 $^{b)}$(wt%)	$1\text{-}C_6^{=c)}$(wt%)	C_8 $^{d)}$(wt%)	$1\text{-}C_8^{=e)}$(wt%)
1	0.53	22.10	83.27	65.62	96.68
2	1.65	27.47	87.06	63.12	99.33

a) 10^6 g/mol Cr.h; b) percentage of C_6 cut in oligomeric mixture; c) percentage of 1-olefins in the C_6 cut; d) percentage of C_8 cut in oligomeric mixture; e) percentage of 1-olefins in the C_8 cut. Solvent: toluene; reaction time: 30 min. Al/Cr molar ratio=540; reaction temperature: 60℃; reaction pressure: 3.0 MPa. $1\text{-}C_6^=$: 1-hexene; $1\text{-}C_8^=$: 1-octene.

2.2 The effect of reaction temperature on catalytic properties

The catalytic properties of catalysts **1** and **2** for ethylene tetramerization are strongly affected by reaction temperature, as shown in Table 2. With reaction temperature rising, the activity of the catalysts increased, the selectivity and purity of C_8 cut decreased while

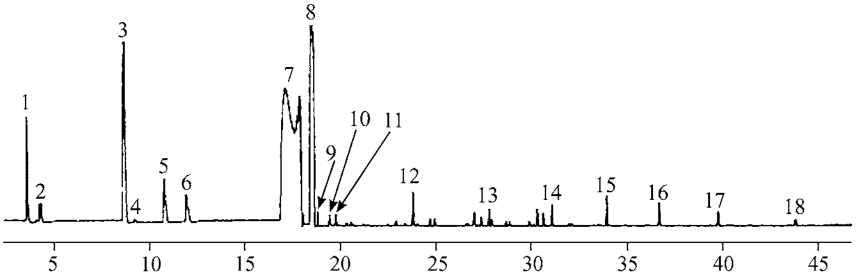

Fig. 2. The chromatogram of ethylene tetramerization products. 1, Ethylene; 2, 1-butylene; 3, 1-hexene; 4, n-hexane; 5, methyl cyclopentane; 6, methylene cyclopentane; 7, toluene (reaction solvent); 8, 1-octene; 9, 1-octane; 10, octadiene; 11, 2-octene; 12, 1-decene; 13, 1-dodecene; 14, 1-tetradecene; 15, 1-hexadecene; 16, 1-octadecene; 17, C20 1-alkene; 18, C22 1-alkene.

Table 2 The effect of reaction temperature on catalytic activity and product selectivity

Ligand	Temperature (℃)	Al/Cr	Activity $^{a)}$	C_6 $^{b)}$ (wt%)	$1\text{-}C_6^{=\ c)}$(wt%)	C_8 $^{d)}$(wt%)	$1\text{-}C_8^{=\ e)}$(wt%)
1	60	180	0.89	17.17	79.71	72.52	97.87
1	70	180	1.12	29.93	90.31	57.20	93.59
2	60	540	1.65	27.47	87.06	63.12	99.33
2	80	540	2.11	39.12	93.98	24.28	90.11

a)—e) The conditions and annotation are the same as in Table 1.

those of C_6 cut increased. These results indicate that when the temperature is elevated, the rate of chain transfer increases more than that of propagation, resulting the product with lower molecular weight.

2.3 The effect of reaction pressure on catalytic properties

The effect of reaction pressure on catalytic properties is shown in Table 3. Improving ethylene pressure dramatically increased catalytic activity, the selectivity of C_6 and C_8 changed a little and the purity of $1\text{-}C_8^{=}$ 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 induces the increase of catalytic activity and purity of $1\text{-}C_8^{=}$.

Table 3 The effect of reaction pressure on catalytic activity and product selectivity

Ligand	Pressure (MPa)	Activity a)	C_6 b) (wt%)	$1\text{-}C_6^{=}$ c) (wt%)	C_8 d) (wt%)	$1\text{-}C_8^{=}$ e) (wt%)
1	3.0	1.12	29.93	90.31	57.20	93.59
1	4.0	1.44	29.94	88.55	61.69	99.54

a)—e) The conditions and annotation are the same as in Table 1.

2.4 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 4. In the conditions used, the catalytic activity decreased as the ratio of Al/Cr increased from 180 to 540. The catalyst deactivation may be explained by the excess reduction of the catalytic active species with excess MAO. The chain transfer to aluminum results in the decrease of C_8 cut selectivity while increasing selectivity of C_6 cut[12].

Table 4 The effect of Al/Cr mole ratio on catalytic activity and product selectivity

Ligand	Al/Cr	Activity a)	C_6 b) (wt%)	$1\text{-}C_6^{=}$ c) (wt%)	C_8 d) (wt%)	$1\text{-}C_8^{=}$ e) (wt%)
1	180	0.89	17.17	79.71	72.52	97.87
1	540	0.53	22.10	83.27	65.62	96.68

a)—e) The conditions and annotation are the same as in Table 1.

3 Conclusion

In combination with Cr(Ⅲ) and MAO, two novel PNP ligands generate active catalytic systems respectively which can tetramerize ethylene to 1-octene with both high catalytic activity and high selectivity. The ligand structure, reaction temperature, reaction pressure and Al/Cr molar ratio have very important effect on catalytic properties. It was found that with the increase of alkyl bridge length, the catalytic activity increased, the selectivity and purity of 1-octene remained almost unchanged. With the increase of reaction temperature, the catalytic activity increased, but the selectivity and purity of 1-octene decreased. The increasing reaction pressure led to increasing catalytic activity, selectivity and purity of 1-octene. Excess MAO may decrease the catalytic activity, the selectivity and purity of 1-octene. There is a little PE in products, it's content can be controlled under 1 percent by decreasing the impurity content in stock.

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