



Research paper

Novel nickel complexes with hyperbranched structure: Synthesis, characterization and performance in ethylene oligomerization



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ABSTRACT

Two novel nickel complexes with hyperbranched structure were synthesized with 1.0 generation hyperbranched polyamine molecules (1.0G), salicylaldehyde and anhydrous nickel chloride as materials via the Schiff's base and the complexation reactions. The structures of the novel hyperbranched ligands and their nickel complexes were characterized by FT-IR, ¹H NMR, UV, ESI-MS and elemental analysis. The hyperbranched nickel complexes were evaluated as catalyst precursors for ethylene oligomerization after being activated with methylaluminoxane (MAO), diethylaluminum chloride (Et₂AlCl) and ethylaluminum sesquichloride (EASC). The influence of Al/Ni ratio, temperature and ethylene pressure on ethylene oligomerization was also investigated using the novel hyperbranched nickel complexes as pre-catalysts and MAO as co-catalyst. The catalytic activities of the two hyperbranched nickel complexes with dodecyl and octadecyl as cores (R₁₂-complex and R₁₈-complex) were 2.33 × 10⁵ g/(mol Ni·h) and 1.23 × 10⁵ g/(mol Ni·h), respectively, and the selectivities for C₈₊ oligomers of R₁₂-complex and R₁₈-complex were 56.16% and 88.64% respectively, when the Al/Ni molar ratio was 500:1, the temperature was 25 °C, the pressure of ethylene was 0.5 MPa and the co-catalyst was MAO. The catalytic activities and product distribution were largely dependent on the nature of the co-catalysts and the structures of nickel complexes. The catalytic activities decreased with increasing of the length of alkyl chain of the hyperbranched nickel complexes.

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1. Introduction

Olefins are extensively used in the preparation of lubricants, plasticizers, detergents, surfactants, et al. [1,2]. Ethylene oligomerization is one of the most important catalytic processes for the production of olefins. Since the discovery of Shell Higher Olefins Processing (SHOP) nickel based catalysts, there have been considerable interests in the development of the oligomerization and polymerization of olefins based on the late transition metal catalysts. Compared with the traditional Ziegler-Natta/metalocene catalysts, the late transition metal catalysts could tolerate a range of polar functional groups and even water. Various studies demonstrated the catalyst structure, choice of co-catalyst and reaction conditions affected the catalytic activity and selectivity, and the ligand structure plays a major role [3].

Many studies focused on the design of the catalyst ligand. Since the discovery of α -diimine nickel complexes as highly active pre-complexes in ethylene polymerization [4], various bi-dentate and tri-dentate ligands have been designed and developed to improve

the catalytic performance of the late transition metal catalysts [5–9]. For instance, Sun and co-workers have investigated the properties of the bi-dentate nickel complexes bearing *NO* ligands [10,11]. Upon activation with EASC or Et₂AlCl, all nickel pre-catalysts displayed good catalytic activity for ethylene dimerization. Their group have also studied the tri-dentate nickel complexes bearing *NNN* ligands [12]. On activation with Et₂AlCl, the nickel complexes exhibited moderate catalytic activities for ethylene oligomerization. Bi-dentate salicylaldehyde imine ligands have attracted great attention because the monoanionic ligand structures were easy to access and the O-containing aromatic ring could be modeled by adding substituent groups with different steric hindrance. Song and co-workers [13] synthesized a series of salicylaldehyde imine nickel based catalysts, and the results for ethylene oligomerization showed that catalytic activity was significantly improved with the increase of the ligand steric hindrance. Zohuri and co-workers [14] synthesized nickel based FI catalysts with different salicylaldehyde imine ligands and studied the ethylene polymerization behavior of the nickel catalysts after activation with methylaluminoxane (MAO). The results indicated that substituents on the arene moiety or the backbone of the ligand influenced the activities during the polymerization. Mu and

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co-workers [15] synthesized a series of neutral nickel complexes based on 2-nitrophenyl-, pentafluorophenyl-, and 2-methoxyphenyl-substituted salicylaldimine ligands, and the results showed that all the complexes with electron-withdrawing groups proved to be highly active single-component catalysts, producing polymer with moderate molecular weights in the ethylene oligomerization process. Malgas and co-workers [16] synthesized two types of dendritic salicylaldimine nickel catalysts with well-defined structures using first-generation and second-generation dendrimers, and the catalytic results showed that the highest activity of 4.68×10^5 g/(mol Ni·h) was obtained under activation with methylaluminoxane (MAO) as a co-catalyst. Han and co-workers [17] synthesized a binuclear heteroligated titanium catalyst based on phenoxyimine ligand and they found the binuclear monophenoxyimine catalyst exhibited higher catalytic activity and incorporated more α -olefin than its mononuclear analogue in the copolymerization.

During the past few years, much effort has been devoted towards the design of the dendritic late transition metal catalysts and their application in ethylene oligomerization reactions [18–20]. In 2013, we synthesized a novel dendritic salicylaldimine nickel-based catalyst with 1.0 generation dendritic polyamide-amine as bridged group and used in ethylene oligomerization, and the results showed that the ethylene oligomerization activity reached up to 4.80×10^6 g/(mol Ni·h) upon MAO activation and the major products were short-chain oligomers of C₄ and C₆ [21]. However, we observed that the dendrimer catalyst with symmetrical structure had a poor solubility and was not easily synthesized. In order to overcome the shortcomings of the symmetric dendritic catalyst, we have synthesized a novel hyperbranched bridged salicylaldehyde-imine nickel-based catalyst with unsymmetrical structure, and ethylene oligomerization performance showed the catalyst possessed a middle catalytic activity of 5.59×10^5 g/(mol Ni·h) with a selectivity for higher olefins (C₁₀–C₁₈) of 91% [22]. One of the advantages of the catalysts based on hyperbranched molecules is the possibility of combining the best properties of homogeneous and heterogeneous catalyst in one system. Their stable structure is more suitable for recycling than linear soluble polymer-supported catalysts. For example, hyperbranched catalysts can potentially be separated from the products via ultrafiltration. Based on these works, we synthesized two salicylaldehyde imine nickel based complexes with hyperbranched structure and long alkyl chain to gain the role of the alkyl chain in ethylene oligomerization in this paper, and moreover investigated the effect of reaction conditions on the catalytic performance.

2. Experimental

2.1. Materials and general instrumentations

Manipulations of air and moisture sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene was dried by refluxing over sodium/benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 10 wt% in toluene) was purchased from Sigma-Aldrich (China). Et₂AlCl (25 wt% in toluene) and ethylaluminum sesquichloride (EASC, 25 wt% in toluene) were purchased from Aladdin (China). Toluene and methanol were provided by Tianjin Kermel Chemical Reagent Co., Ltd (China). Salicylaldehyde was obtained from Tianjin Guangfu Fine Chemical Research Institute (China). 1.0G hyperbranched macromolecules (R₁₂-1.0G) with 1-dodecylamine as core and 1.0G hyperbranched macromolecules (R₁₈-1.0G) with 1-octadecylamine as core were synthesized in our laboratory [23].

IR spectra were recorded on a Nicolet FT-IR 750 infrared spectrometer using the KBr pellets method. ¹H NMR spectra were obtained on a Varian 400 MHz in CDCl₃ as the solvents and tetramethylsilane (TMS) as the internal standard. Absorbency of the ligand and its complex were determined using a UV-1700 UV-vis spectrophotometer. Mass spectral (MS) data were collected on a Bruker Apex Ultra 70 FTMS using electrospray ionization (ESI) as ion-source. Gas chromatography (GC) analyses were conducted on a Fuli GC 9720 equipped with an flame ionization detector (FID) and a 50 m (0.2 mm i.d., 0.5 μ m film thickness) HP-PONA column.

2.2. Synthesis of novel nickel complexes with hyperbranched structure

2.2.1. Synthesis of novel hyperbranched ligands

R₁₂-1.0G (4.13 g, 0.01 mol) and anhydrous sodium sulfate (3 g) were dissolved in 40 mL purified methanol at 25 °C in a flask under nitrogen atmosphere. Salicylaldehyde (4.37 mL, 0.044 mol) was added to the solution dropwise and the reaction mixture was allowed to stir under reflux for 12 h at 78 °C. The mixture was filtered to yield the yellow precipitate, and the yellow precipitate was washed by 100 mL diethyl ether. The yellow solid was dried under vacuum at 50 °C to afford the novel hyperbranched ligand with R₁₂-1.0G as bridged group (R₁₂-ligand). Yield: 55%. ¹H NMR (CDCl₃, δ ppm): 0.87–0.91 (t, 3H, –CH₃), 0.99–1.65 (m, 20H, –(CH₂)₁₀–), 2.20–2.26 (m, 4H, –CH₂CO–), 2.57–2.67 (m, 4H, –NCH₂–), 2.80–2.85 (m, 2H, –CH₂N–), 3.03–3.15 (m, 4H, N–CH₂–C–CO), 3.77–3.94 (m, 4H, –CH₂N=), 4.35–4.42 (m, 2H, –CONH–), 5.22 (s, 2H, –OH), 6.86–7.34 (m, 8H, –Ar–H), 8.36 (s, 2H, –N=CH–). Anal. Calcd. for C₃₆H₅₅N₅O₄: C, 69.53; H, 8.91; N, 11.26. Found: C, 69.73; H, 8.55; N, 11.49. ESI-MS (*m/z*): 622.3 [M+H]⁺, 508.3 [M–C₈H₁₇]⁺, 453.1 [M–C₁₂H₂₅]⁺, 202.7 [M–C₇H₆ON]²⁺.

The synthetic procedure of the novel hyperbranched ligand with R₁₈-1.0G as bridged group (R₁₈-ligand) was similar to that described for R₁₂-ligand, and the materials of R₁₈-ligand were R₁₈-1.0G (4.97 g, 0.01 mol) and salicylaldehyde (4.37 mL, 0.044 mol), respectively. Yield: 53%. ¹H NMR (CDCl₃, δ ppm): 0.87–0.90 (t, 3H, –CH₃), 0.98–1.57 (m, 32H, –(CH₂)₁₆–), 2.20–2.26 (m, 4H, –CH₂CO–), 2.58–2.68 (m, 4H, –NCH₂–), 2.80–2.85 (m, 2H, –CH₂N–), 3.03–3.14 (m, 4H, N–CH₂–C–CO), 3.79–3.94 (m, 4H, –CH₂N=), 4.36–4.41 (m, 2H, –CONH–), 5.22 (s, 2H, –OH), 6.86–7.34 (m, 8H, –Ar–H), 8.36 (s, 2H, –N=CH–). Anal. Calcd. for C₄₂H₆₇N₅O₄: C, 71.45; H, 9.57; N, 9.92. Found: C, 71.12; H, 9.54; N, 9.97. ESI-MS (*m/z*): 706.5 [M+H]⁺, 244.8 [M–2C₇H₆O]²⁺.

2.2.2. Synthesis of novel hyperbranched nickel complexes

The R₁₂-ligand (0.3 g, 0.46 mmol) and anhydrous nickel chloride (0.073 g, 0.56 mmol) were dissolved in 15 mL methanol under nitrogen atmosphere. The reaction mixture was stirred for 24 h at 25 °C. 150 mL Diethyl ether was added to the mixture, and the green solid formed. The solid was collected by filtration and washed with cold ether (100 mL). The solid was dried under vacuum to obtain the novel hyperbranched complex with R₁₂-1.0G as bridged group (R₁₂-complex). Yield: 94%. Anal. Calcd. for C₃₆H₅₃N₅NiO₄: C, 63.72; H, 7.87; N, 10.32. Found: C, 64.07; H, 7.80; N, 10.54. ESI-MS (*m/z*): 678.3 [M+H]⁺, 622.4 [M–Ni]⁺.

The synthetic procedure of the novel hyperbranched complex with R₁₈-1.0G as bridged group (R₁₈-complex) was similar to that described for R₁₂-complex, and the materials of R₁₈-complex were R₁₈-ligand (0.3 g, 0.46 mmol) and anhydrous nickel chloride (0.073 g, 0.56 mmol), respectively. Yield: 93%. Anal. Calcd. for C₄₂H₆₅N₅NiO₄: C, 66.14; H, 8.59; N, 9.18. Found: C, 64.18; H, 8.42; N, 8.90. ESI-MS (*m/z*): 762.1 [M+H]⁺, 707.7 [M–Ni]⁺.

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