



Nickel complexes based on hyperbranched salicylaldimine ligands: Synthesis, characterization, and catalytic properties for ethylene oligomerization



Jun Wang, Na Zhang, Cui Qin Li*, Wei Guang Shi, Zhi Yu Lin

Provincial Key Laboratory of Oil & Gas Chemical Technology, College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, Heilongjiang Province, China

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ABSTRACT

A series of new nickel complexes based on hyperbranched salicylaldimine ligands have been prepared in good yields and characterized by FT-IR, ^1H NMR, UV, ESI-MS and TGA. Upon activation with methylaluminumoxane (MAO) or diethylaluminum chloride (DEAC), these new precatalysts showed high activity in ethylene oligomerization, and notably remarkably high selectivity of high carbon olefins in the presence of DEAC. The catalytic performance was substantially affected by the solvent type, reaction conditions and the structure of catalyst. Under optimized conditions, precatalyst C1 led to TOF = 13.65×10^5 g/mol Ni·h and 21.53% selectivity for high carbon olefins. The result of thermal analysis revealed that the complex C1 was stable up to 298.4 °C. The research result of the kinetics of ethylene oligomerization found that the pressure drop of ethylene consumption sharply increased in the initial stage, however with the prolonged reaction time, the pressure drop of ethylene consumption varied a little.

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1. Introduction

α -olefins can undergo many transformations, which include hydrogenation, cracking, cyclization, isomerization, oligomerization and polymerization reactions [1]. The oligomerization of ethylene is an important catalytic process for the production of linear α -olefins, which are important substances extensively used in the preparation of lubricants, plasticizers, surfactants, and oil chemicals, as well as comonomers for the synthesis of linear low-density polyethylene, therefore this process receives great interest both in academia and industry fields [2–4]. Since the discovery of Shell Higher Olefins Process (SHOP) nickel (II) based catalysts, metal nickel (II) complexes have attracted much attention because they are less sensitive to protonic solvents and polar monomers [5–9].

Hyperbranched macromolecules are a relatively new class of macromolecules, which have attracted significant attention due to their unique architectures, special chemical properties and physical properties since Flory's seminal theoretical reported in 1952 [10].

However the very first synthesis of branched system was reported by Vögtle and co-worker [11] until 1978, and used the term "cascade macromolecules". The innovative work of Vögtle led to the synthesis of the first macromolecular hyperbranched polyphenylene system that was reported in 1990 by Kim and Webster [12–14]. Subsequently numerous hyperbranched macromolecules with different structure were synthesized [15–23]. Metallohyperbranched molecules can be obtained by incorporating metal ions into infrastructure of hyperbranched molecular either as cores, branching centres, arm connectors or termini. Metallohyperbranched molecules have applications in a large number of areas such as drug delivery, molecular electronics, sensors and catalysis.

We previously reported the synthesis of hyperbranched nickel complex derived from 1.0 generation (1.0G) hyperbranched salicylaldimine ligand. The complex was evaluated as a catalyst precursor in ethylene oligomerization with MAO as a co-catalyst. The results showed that the complex possessed a middle catalytic activity of 5.59×10^5 g/mol·Ni·h with a selectivity for high carbon olefins (C_{10} – C_{18}) of 91% [24]. Based on above study, we designed and synthesized a series of novel hyperbranched salicylaldimine nickel complexes in this paper. The influence of the catalytic systems and catalytic conditions on the catalytic activity and products

* Corresponding author.

E-mail address: dqpilicuiqin@126.com (C.Q. Li).

distribution were also studied.

2. Experimental section

2.1. Materials and general considerations

All synthetic manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene, cyclohexane and chlorobenzene were analytical grade and dried by refluxing over sodium/benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 10 wt% in toluene) was purchased from Sigma-Aldrich. Diethylaluminum chloride (DEAC, 25 wt% in hexane) were obtained from Aladdin and used as received. Salicylaldehyde was provided by Tianjin Guangfu Fine Chemical Industry Research Institute. Nickel Chloride Hexahydrate was purchased from Tianjin Jizhun chemical reagent co., Ltd. 1,4-butanediamine, 1,6-hexamethylenediamine and 1,8-octanediamine were obtained from Tianjin Kermel Chemical Reagent co., Ltd. The above reagents were used without any further purification. 1.0G hyperbranched macromolecules were synthesized according to the literature procedures [25] and the yields of them were above 80%.

Infrared spectra were recorded in a KBr disc matrix using a Bruker Vector 22 IR spectrophotometer over the range of 4000–450 cm^{-1} . $^1\text{H-NMR}$ spectra were recorded with Bruker-400 MHz NMR at 400 MHz in CDCl_3 with tetramethyl silane (TMS) as an internal reference. The UV–visible spectra were carried out on a UV-1700 ultraviolet–visible spectrophotometer by using methanol as a solvent. Electrospray ionization mass spectrometry (ESI-MS) data were collected on a micrOTOF-Q II mass spectrometer. The thermal gravimetric analysis (TGA) was carried out on a Diamond TG/DTA Perkin-Elmer SII Instrument over the range of 28–800 $^\circ\text{C}$ with the heating rate of 10 $^\circ\text{C}/\text{min}$. Gas chromatography (GC) analyses of oligomers were performed on a Fuli GC9720 equipped with a flame ionization detector (FID) and a 50 m (0.2 mm i.d., 0.5 μm film thickness) HP-PONA column.

2.2. Synthesis of ligands

Methanol was added to the mixture of 1.0G hyperbranched macromolecule S1 (4.69 g, 0.01 mol) and Na_2SO_4 (3 g) which was added to remove the water in the Schiff base reaction under a nitrogen atmosphere at 25 $^\circ\text{C}$ and stirred for 15 min, then the salicylaldehyde (4.30 mL, 0.04 mol) was added dropwise to the solution. The mixture was refluxed for 12 h at 65 $^\circ\text{C}$. The mixture was filtered to remove Na_2SO_4 and attained the ligand solution. The precipitate was obtained after the ligand solution crystallized for 15 d at -30°C . The resulting precipitate was filtered off, and then washed three times with ether. The product was dried in vacuum to afford the ligand L1 as a yellow powder in 24% yield (Scheme 1). IR (KBr, cm^{-1}): 3414 (s), 2917 (s), 1635 (s), 1581 (w), 1436 (m), 1280 (m), 753 (m). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ : 0.874 (t, 3H, CH_3), 1.228 (m, 14H, CH_2), 1.413 (m, 2H, CH_2), 1.572 (m, 2H, CH_2), 1.680 (m, 2H, CH_2), 2.405 (m, 4H, CH_2), 2.714 (t, 2H, CH_2), 2.321 (t, 4H, CH_2), 6.860 (m, 2H, NH), 3.241 (m, 4H, CH_2), 3.582 (t, 4H, CH_2), 8.312 (s, 2H, CH), 7.288 (d, 2H, Ar-H), 6.976 (t, 2H, Ar-H), 7.258 (t, 2H, Ar-H), 6.935 (d, 2H, Ar-H), 7.216 (s, 2H, OH). λ_{max} (nm): 231, 252, 315.

Ligand L2 was prepared according to the method described for L1 using 1.0G hyperbranched macromolecule S2 (5.25 g, 0.01 mol) and salicylaldehyde (4.30 mL, 0.04 mol). Ligand L2 was obtained as a yellow powder in 25% yield. IR (KBr, cm^{-1}): 3301 (s), 2917 (s), 1639 (s), 1424 (m), 1582 (w), 1274 (m), 751 (m). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ : 0.875 (t, 3H, CH_3), 1.229 (m, 14H, CH_2), 1.413 (m, 2H, CH_2), 1.591 (m, 2H, CH_2), 1.680 (m, 2H, CH_2), 2.406 (m, 4H, CH_2), 2.716 (t, 2H, CH_2), 2.322 (t, 4H, CH_2), 6.861 (m, 2H, NH), 3.242 (m,

4H, CH_2), 3.583 (t, 4H, CH_2), 8.313 (s, 2H, CH), 7.288 (d, 2H, Ar-H), 6.989 (t, 2H, Ar-H), 7.260 (t, 2H, Ar-H), 6.915 (d, 2H, Ar-H), 7.213 (s, 2H, OH). λ_{max} (nm): 224, 253, 314.

Ligand L3 was prepared according to the method described for L1 using 1.0G hyperbranched macromolecule S3 (5.81 g, 0.01 mol) and salicylaldehyde (4.30 mL, 0.04 mol). Ligand L2 was obtained as a yellow powder in 19% yield. IR (KBr, cm^{-1}): 3300 (s), 2916 (s), 1638 (s), 1423 (m), 1581 (w), 1278 (m), 751 (m). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ : 0.886 (t, 3H, CH_3), 1.226 (m, 14H, CH_2), 1.413 (m, 2H, CH_2), 1.571 (m, 2H, CH_2), 1.698 (m, 2H, CH_2), 2.417 (m, 4H, CH_2), 2.734 (t, 2H, CH_2), 2.339 (t, 4H, CH_2), 6.865 (m, 2H, NH), 3.254 (m, 4H, CH_2), 3.583 (t, 4H, CH_2), 8.314 (s, 2H, CH), 7.293 (d, 2H, Ar-H), 7.046 (t, 2H, Ar-H), 7.263 (t, 2H, Ar-H), 6.921 (d, 2H, Ar-H), 7.228 (s, 2H, OH). λ_{max} (nm): 226, 253, 316.

2.3. Synthesis of metal complexes

The methanol solution (15 mL) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (4.75 g, 0.02 mol) was added dropwise to the methanol solution (15 mL) of L1 (5.31 g, 0.01 mol) under nitrogen atmosphere. The reaction mixture was stirred for 24 h at 25 $^\circ\text{C}$. The precipitate was obtained after ether added to the resultant solution. The resulting precipitate was filtered off, washed three times with ether and dried in vacuum to furnish the pure product as a green powder in 80% yield (Scheme 1). IR (KBr, cm^{-1}): 3260 (w), 2925 (s), 1628 (m), 1474 (m), 1315 (m), 759 (m). λ_{max} (nm): 221, 240. ESI-MS: m/z : 734 $[\text{M}+\text{H}]^+$.

Complex C2 was prepared from ligand L2 (5.87 g, 0.01 mol) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (4.75 g, 0.02 mol) following the procedure described for complex C1 as a green powder in 76% yield. IR (KBr, cm^{-1}): 3407 (w), 2925 (s), 1621 (m), 1447 (m), 1317 (m), 757 (m). λ_{max} (nm): 223, 239 ESI-MS: m/z : 791 $[\text{M}+\text{H}]^+$.

Complex C3 was prepared from ligand L3 (6.43 g, 0.01 mol) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (4.75 g, 0.02 mol) following the procedure described for complex C1 as a green powder in 71% yield. IR (KBr, cm^{-1}): 3385 (w), 2925 (s), 1621 (m), 1446 (m), 1315 (m), 756 (m). λ_{max} (nm): 222, 241. ESI-MS: m/z : 847 $[\text{M}+\text{H}]^+$.

2.4. General procedure for ethylene oligomerization reaction

Ethylene oligomerization reactions were carried out in a 250 mL stainless steel reactor with magnetic stirring. The reactor was heated under vacuum for 2 h at 160 $^\circ\text{C}$ and subsequently allowed to cool to the room temperature. The reactor was flushed with ethylene three times. Solvent, the desired amount of co-catalyst, and solution of the metal complex (0.7 $\mu\text{mol}/\text{mL}$, 10 mL) (The total volume was 50 mL) were added to the reactor in this order under an ethylene atmosphere, when the desired reaction temperature was reached, the ethylene pressure was increased to desired value, and maintained at this level by constant feeding of ethylene. After 30 min, the reaction was stopped by releasing the excess ethylene. A small amount of the reaction solution was collected, the reaction was terminated by the addition of 5% aqueous hydrogen chloride, and then this mixture was analyzed by gas chromatography (GC) to determine the distribution of oligomers obtained.

3. Results and discussion

3.1. Characterization of metal complexes

3.1.1. FT-IR spectroscopy

IR spectra for the hyperbranched salicylaldimine ligands and metal complexes are shown in Fig. 1. For the ligands, the absorption peaks at around 3301 cm^{-1} were due to the stretching vibration of the N-H group. The characteristic peak at around 2917 cm^{-1}

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