Journal of Molecular Catalysis A: Chemical 398 (2015) 289–296

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

[ONNO]-type oxovanadium(V) complexes containing amine pyridine bis(phenolate) ligands: synthesis, characterization and catalytic behavior for ethylene (co)polymerization

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ARTICLE INFO

Article history:
Received 9 October 2014
Received in revised form
20 December 2014
Accepted 23 December 2014
Available online 5 January 2015

Keywords:
Vanadium catalyst
Homogeneous catalysis
Ethylene (co)polymerization

ABSTRACT

A series of oxovanadium(V) complexes bearing dianionic [ONNO] chelate ligands 2-[bis(3-R^1-5-R^2-2 -hydroxybenzyl) aminomethyl]pyridine (**2a**: R^1 = ^{t}Bu, R^2 = H; **2b**: R^1 = CF_3, R^2 = H; **2c**: R^1 = OCH_3, R^2 = H; **2d**: R^1 = R^2 = ^{t}Bu) and 2-[bis(3-R^1-5-R^2-2 -hydroxybenzyl) aminoethyl]pyridine (**2e**: R^1 = R^2 = ^{t}Bu) have been synthesized by reacting $VO(O^nPr)_3$ with 1.0 equiv. of the ligands in CH_2Cl_2. All these complexes were characterized by ^1H, ^{13}C, ^{51}V NMR spectra and elemental analysis. X-ray structural analysis for **2d** revealed a six-coordinate distorted octahedral geometry around the vanadium center in the solid state. It was observed that these complexes existed as a mixture of two isomers, and the main isomer had the oxo moiety in *trans* configuration to the tripodal nitrogen atom. In the presence of Et_2AlCl and CCl_3COOEt, these complexes displayed high catalytic activities for ethylene polymerization even at elevated reaction temperature, depending on ligand structures. The resultant polymers possessed high molecular weights and unimodal molecular weight distributions, indicative of a single active site nature. In addition, copolymerizations of ethylene and norbornene using precatalysts **2a**–**e** were also investigated, and the observed catalytic activity was nearly comparable with that for ethylene homopolymerization. When the concentration of comonomer in the feed amounted to 3.0 mol/L, a NBE incorporation up to 41.5% could be achieved. Other reaction parameters that influenced the polymerization behavior, such as reaction temperature and Al/V (molar ratio), are also examined in detail.

1. Introduction

The development of well-defined single-site transition metal catalysts for olefin polymerization has been intense in recent years since the properties of the resultant polymers can be well controlled by catalyst structures [1–5]. Vanadium complexes, as one of the first homogeneous Ziegler–Natta catalysts, have been very attractive and extensively used in the production of high molecular weight polyethylene, ethylene/propylene copolymers, ethylene/propylene/diene elastomers [6–8]. While deactivation due to the reduction to low-valent, or inactive species is associated with vanadium catalysts [9–10], the introduction of ancillary ligands, especially polydentate ancillary ligands, to stabilize active vanadium(V) species has proved to be a powerful approach to keep vanadium in high-oxidation, which subsequently prolongs the catalyst life-time [11–23]. For example, Gibson reported that bis(benzimidazole) amine vanadium(V) catalysts exhibited high activity and fine comonomer incorporation toward ethylene/norbornene copolymerization even at high reaction temperature [11]. Redshaw and co-workers described a program of screening high valent vanadyl systems containing various aryloxides ligands for efficient application in ethylene polymerization and ethylene/propylene copolymerization [13–15]. Nomura and co-workers obtained a series of vanadium (V) imido complexes with aryloxide coligands as efficient catalysts for olefin (co)polymerization, some of which exhibited remarkable catalytic activities, excellent comonomer incorporating ability at high temperature [17–18]. Our group reported a series of vanadium(V) complexes bearing trianionic tetradentate amine trihydroxy ligands which displayed remarkable catalytic activities for olefin polymerizations and were capable of keeping high productivity within 30 min [19a].

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http://dx.doi.org/10.1016/j.molcata.2014.12.016

Tripodal [ONNO]-H_2 are easily synthesized and highly versatile ligands, whose steric and electronic effects can be readily tuned by changing the substituents in aryloxo or the bridgehead nitrogen. This ligand family was successfully introduced by Kol et al. for group IV metal in the report of highly isospecific living polymerization of l-hexane [24,25]. Recently, we developed a series of [ONN]-type monoanionic amine pyridine(s) phenalate-based oxovanadium(V) complexes which showed considerably high catalytic activities for ethylene (co)polymerization and displayed good capability for NBE incorporation [19b]. Considering that additional anionic aryloxide chelating group would be beneficial for stabilizing catalytically active species and thus improved the catalytic performance for olefin polymerization, dianionic amine pyridine bis(phenolate) [ONNO] compounds were introduced as ancillary ligands. In this study, a series of novel oxovanadium(V) complexes chelating dianionic 2-[bis(3-R_1-5-R_2-2-hydroxybenzyl) aminomethyl]pyridine (**2a**: $R^1={}^t$Bu, R^2 = H; **2b**: $R^1=CF_3$, R^2 = H; **2c**: $R^1=OCH_3$, R^2 = H; **2d**: $R^1=R^2={}^t$Bu) and 2-[bis(3-R^1-5-R^2-2-hydroxybenzyl) aminoethyl]pyridine (**2e**: $R^1=R^2={}^t$Bu) were synthesized and characterized. Upon treatment with Et_2AlCl and CCl_3COOEt, these complexes not only displayed high catalytic activities for ethylene polymerization even at high reaction temperature, but also exhibited favorable capability for ethylene/NBE (co)polymerization, affording copolymers with NBE content up to 41.5%.

2. Experimental

2.1. General procedures and materials

Ethyl trichloroacetate (ETA) were purchased from Aldrich, dried over calcium hydride at room temperature and then distilled. $VO(O^nPr)_3$, phenol compounds, and amine compounds were purchased from Aldrich. Diethylaluminium chloride was obtained from Albemarle Corp.

2.2. Procedure for ethylene (co)polymerization

Ethylene polymerizations were conducted in a 300 mL scale stainless steel autoclave with a mechanical stirrer. The reactor was cleared and baked under nitrogen for 24 h at 150° C and subsequently cooled to the required temperature before the polymerization. Then, toluene (30 mL) and the prescribed amount of comonomer, a solution of Et_2AlCl in toluene, a solution of ETA in toluene and a toluene solution containing vanadium complex were introduced into the autoclave via a syringe. Additional toluene was poured into this system to keep a total volume of 50 mL. Soon after the addition, the reaction apparatus was then filled with ethylene of the prescribed pressure. The mixture was magnetically stirred until the prescribed reaction time. Then, the reactor was vented, and the resulted mixture was poured into EtOH/HCl (95/5). The resultant polymer was collected on a filter paper by filtration, washed with EtOH and dried under vacuum at 60 °C for 10 h.

2.3. Synthesis of amine pyridine bis(phenolate) ligands (1a–e)

A series of [ONNO]H_2 ligands 2-[bis(3-R^1-5-R^2-2-hydroxybenzyl) aminomethyl]pyridine bearing different substituents on R^1 and R^2 positions (**1a**: $R^1={}^t$Bu, R^2 = H; **1b**: $R^1=CF_3$, R^2 = H; **1c**: $R^1=OCH_3$, R^2 = H; **1d**: $R^1=R^2={}^t$Bu) and 2-[bis(3-R^1-5-R^2-2-hydroxybenzyl) aminoethyl]pyridine (**1e**: $R^1=R^2={}^t$Bu) were prepared according to literature procedures (see Supporting information) [24–26]

2.4. Synthesis of oxovanadium(V) complexes (2a–f)

The precedure was manipulated in glove-box filled with nitrogen. To a stirred solution of $VO(O^nPr)_3$ (244 mg, 1.0 mmol) in dried CH_2Cl_2 (15 mL) was slowly added a solution of ligand **1a** (432 mg, 1.0 mmol) in CH_2Cl_2 (20 mL). After stirring for 8 h at room temperature, the dark blue reaction mixture was concentrated to about 2 mL. Crystallization by diffusion of *n*-hexane (12 mL) into the clear solution yielded black crystals of **2a** (457 mg, 67%). Compounds **2b-d** were prepared according to the same procedure.

2a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 5.4 Hz, 1H, Ar-*H*), 7.39 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 7.08 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.05–6.98 (m, 1H, Ar-*H*), 6.93 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 6.63 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 6.58 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 5.23 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.60 (d, *J* = 12.5 Hz, 2H, NC*H*$_2$), 3.79 (s, 2H, NC*H*$_2$), 3.38 (d, *J* = 12.5 Hz, 2H, NC*H*$_2$), 1.82 (h, *J* = 7.1 Hz, 2H, C*H*$_2$), 1.36 (s, 18H, C*H*$_3$), 0.91 (t, *J* = 7.4 Hz, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, C_6D_6) δ 156.34, 152.68, 148.45, 138.88, 137.91, 128.13, 127.05, 126.38, 125.35, 119.26, 117.79, 86.12, 60.61, 56.50, 34.92, 30.17, 62.69, 26.10, 10.90. ^{51}V NMR (105 MHz, $CDCl_3$): δ -452.28. Anal. calcd for $C_{31}H_{41}N_2O_4V$: C, 66.89; H, 7.42; N, 5.03. Found: C, 67.03; H, 7.48; N, 4.96.

Complex **2b** was obtained as brown powder in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.7 Hz, 1H, Ar-H), 7.50 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.34 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.22 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.17–7.07 (m, 1H, Ar-*H*), 6.82 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 6.69 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 5.92 (t, *J* = 6.5 Hz, 2H, OC*H*$_2$), 4.66 (d, *J* = 11.2 Hz, 2H, NC*H*$_2$), 3.96 (s, 2H, NC*H*$_2$), 3.86 (d, *J* = 13.5 Hz, 2H, NC*H*$_2$), 2.09–1.96 (m, 2H, C*H*$_2$), 1.13 (t, *J* = 7.4 Hz, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.92, 154.43, 149.08, 138.3, 132.15, 126.89, 126.42, 125.43, 123.60, 123.04, 121.07, 117.41, 90.76, 63.32, 61.44, 63.08, 26.08, 10.67. ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.42 (s). ^{51}V NMR (105 MHz, $CDCl_3$): δ −494.60. Anal. calcd for $C_{25}H_{23}F_6N_2O_4V$: C, 51.74; H, 3.99; N, 4.83. Found: C, 51.89; H, 4.02; N, 4.76.

Complex **2c** was obtained as dark blue crystals in 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 5.3 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 7.21–7.13 (m, 2H, Ar-*H*), 7.01–6.94 (m, 1H, Ar-*H*), 6.76 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 6.63–6.57 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 6.51–6.45 (m, 1H, Ar-*H*), 5.69 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.42–4.35 (m, 2H, NC*H*$_2$), 3.79 (s, 6H, OC*H*$_3$), 3.52–3.41 (m, 4H, NC*H*$_2$), 1.48–1.39 (m, 2H, C*H*$_2$), 0.88 (t, *J* = 7.4 Hz, 3H, C*H*$_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.89, 156.31, 152.63, 148.46, 138.81, 137.92, 128.15, 127.03, 126.32, 125.38, 119.24, 117.77, 86.15, 63.12, 62.60, 55.31, 47.02, 26.14, 10.92.^{51}V NMR (105 MHz, $CDCl_3$): δ −441.10. Anal. calcd for $C_{25}H_{29}N_2O_4V$: C, 59.52; H, 5.79; N, 5.55. Found: C, 59.66; H, 5.83; N, 5.48.

Complex **2d** was obtained as black crystals in 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, *J* = 5.1 Hz, 1H, Ar-*H*), 7.34 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.07 (d, *J* = 2.1 Hz, 2H, Ar-*H*), 6.98 (t, *J* = 6.4 Hz, 1H, Ar-*H*), 6.90 (d, *J* = 2.0 Hz, 2H, Ar-*H*), 6.50 (s, 1H, Ar-*H*), 5.13 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 4.58 (d, *J* = 12.3 Hz, 2H, NC*H*$_2$), 3.74 (s, 2H), 3.35 (d, *J* = 12.4 Hz, 2H, NC*H*$_2$), 1.82 (h, *J* = 7.1 Hz, 2H, C*H*$_2$), 1.36 (s, 18H, C*H*$_3$), 1.24 (s, 18H, C*H*$_3$), 0.91 (t, *J* = 7.4 Hz, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.63, 156.34, 152.57, 148.22, 141.73, 139.84, 138.25, 135.71, 124.52, 122.88, 121.91, 120.10, 85.22, 63.12, 62.83, 56.54, 35.05, 34.38, 30.06, 26.23, 25.96, 10.85. ^{51}V NMR (105 MHz, $CDCl_3$): δ −452.28. Anal. calcd for $C_{39}H_{57}N_2O_4V$: C, 70.04; H, 8.59; N, 4.19. Found: C, 70.10; H, 8.64; N, 4.11.

Complex **2e** was obtained as dark green powder in 72% yield. *Trans*-configuration: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 4.8 Hz, 1H,Ar-*H*), 7.33 (td, *J* = 7.6, 1.4 Hz, 1H, Ar-*H*), 7.23 (d, *J* = 2.2 Hz, 2H, Ar-*H*), 7.02 (d, *J* = 6.2 Hz, 1H, Ar-*H*), 7.01–6.98 (m, 1H, Ar-*H*), 6.92 (d, *J* = 2.1 Hz, 2H, Ar-*H*), 6.48 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 5.54 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 5.01 (d, *J* = 14.3 Hz, 2H, NC*H*$_2$), 3.75 (d, *J* = 14.4 Hz, 2H, NC*H*$_2$), 3.03 (t, *J* = 6.5 Hz, 2H, NC*H*$_2$), 2.74 (m, 2H, NC*H*$_2$), 1.87 (dt, *J* = 14.1, 5.1 Hz, 2H, C*H*$_2$), 1.30 (s, 18H, C*H*$_3$), 1.29 (s, 18H, C*H*$_3$), 1.02 (t, *J* = 7.4 Hz, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.06, 149.76,