



Short Communication

Oligomerization of ethylene using tridentate nickel catalysts bearing ether-pyrazol ligands with pendant O- and S-donor groups

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ARTICLE INFO

Article history:

Received 2 July 2011

Received in revised form 26 August 2011

Accepted 10 September 2011

Available online 17 September 2011

Keywords:

Ni(II) catalysts

Tridentate ligands

Oligomerization

1-butene

ABSTRACT

A series of tridentate pyrazol ligands with pendant O- and S-donor groups (L1–L5) and their corresponding nickel (II) chloride complexes (1–5) were synthesized and fully characterized. All nickel precatalysts, activated with methylaluminoxane (MAO), exhibited high activities for ethylene oligomerization [TOF = $17.1\text{--}75.8 \times 10^3 \text{ mol (ethylene)}(\text{mol}(\text{Ni}))^{-1} \text{ h}^{-1}$] with good selectivities for 1-butene produced (62.9 – 81.3%). The catalytic performance was substantially affected by the ligand environment regarding the pendant oxygen- and sulfur-donor groups, and the substituents on the phenol group. Activation of nickel precatalyst 1 with ethylaluminum sesquichloride ($\text{Et}_2\text{Al}_2\text{Cl}_3$, EASC) instead of MAO produced a significantly better catalyst system than 1/MAO (TOF = 227,000 vs. 30,900 ($\text{mol C}_2\text{H}_4$)·($\text{mol Ni}^{-1} \text{ h}^{-1}$)); however, the 1-butene selectivity was drastically reduced, attaining only 28% with a concomitant production of larger amounts of internal butenes (51.4%) and hexenes (28.2%). Under optimized conditions ([Ni] = $10 \mu\text{mol}$, 30°C , oligomerization time = 20 min, 40 bar ethylene, [Al]/[Ni] = 250), precatalyst 1 led to TOF = 75,800 ($\text{mol C}_2\text{H}_4$)·($\text{mol Ni}^{-1} \text{ h}^{-1}$) and 76.1% selectivity for 1-butene.

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1. Introduction

The oligomerization of ethylene is one of the most important industrial processes to obtain linear α -olefins (LAOs) [1–5]. These substrates have been extensively used for preparing detergents, lubricants, plasticizers, and oil field chemicals or as monomers for copolymers, etc.[6–7] Among classes of catalysts used for the production of α -olefins, nickel complexes containing P,P-, [8–11] P,N-, [12–24] P,O-, [25–32] N,N-, [33–42] or N,O- [43–50] as bidentate chelating ligands are the most frequently studied. More recently, nickel complexes bearing tridentate ligands have attracted much interest owing to their good to excellent performance towards the production of α -olefins [51–69]. In comparison with bidentate complexes, the scope of tridentate nickel complexes are still at the exploratory stage; moreover, the affective factors of the ligands on their catalytic behaviors are still arguable.

We have previously reported on the use of 5- and 6-membered-ring nickel complexes based on tridentate pyrazolyl ligands [70–73] as highly selective and active systems for ethylene oligomerization when activated with alkylaluminum (MAO or AlEt_2Cl). The nickel complexes based on tridentate nitrogen- or oxygen-bridged bis(pyrazolyl) ligands (A in Fig. 1) proved to be highly selective and efficient precatalysts for ethylene dimerization in the presence of methylaluminoxane (MAO) [71]. Substitution of the central nitrogen- or oxygen-donor by a sulfur atom promoted higher catalytic activities.

By changing from the six-membered chelate ring (A in Fig. 1) to the five-membered chelate ring (B in Fig. 1) of the bis(pyrazol) ligand, the activity increases, probably due to the formation of a more rigid and stable structure imposed by this class of ligands. Activation of these nickel complexes with diethylaluminumchloride (DEAC) instead of MAO produced, in general, much more active systems [TOFs varying from 33,900 to 91,000 ($\text{mol C}_2\text{H}_4$)·($\text{mol Ni}^{-1} \text{ h}^{-1}$)], along with lower selectivity for 1-butene (72.0–81.3%) and concomitant production of larger amounts of butenes (18.7–25.7%) [72]. This observation, which is in striking contrast with the aforementioned marked difference with the corresponding MAO-activated systems, could reflect better stabilization of the active species with DEAC than with MAO, possibly thanks to the chlorine atom.

Herein, we wish to report the synthesis and characterization of several new nickel(II) complexes bearing tridentate ether-pyrazolyl ligands with pendant oxygen- and sulfur-donor groups (C in Fig. 1), as well as their catalytic behaviors for ethylene oligomerization. We also discuss the effect of substituents and reaction conditions on their activity and selectivity towards the production of 1-butene.

2. Experimental section

2.1. General procedures

All manipulations were performed using a standard vacuum line and Schlenk techniques under a purified argon atmosphere. All solvents were distilled from the appropriate drying agents under argon

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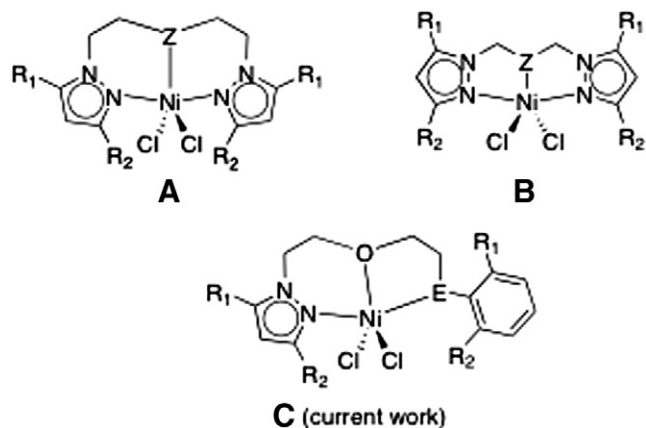


Fig. 1. Models of nickel catalysts based on tridentate pyrazolyl ligands.

before use. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) was used as received. 1-(2-(2-chloroethoxy)ethyl)-3,5-dimethyl-1H-pyrazole [74], and (DME) NiCl_2 [75], (DME = 1,2-dimethoxyethane) were prepared by following literature procedures. Ethylene (White Martins Co.) and argon were deoxygenated and dried through BTS columns (BASF) and activated molecular sieves (3A) prior to use. PMAO-IP (Akzo Nobel, 12.9 wt.% Al solution in toluene) was used as received. EASC (Akzo Nobel) was used with the previous dilution (2.1 wt.% Al solution in toluene). Elemental analyses were performed by the Analytical Central Service of the Institute of Chemistry-UFRGS (Brazil) and are the average of two independent determinations. Infrared spectra were performed on a FT-IR Bruker Alpha Spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 25 °C. Chemical shifts are reported in ppm vs. SiMe_4 and were determined by reference to the residual solvent peaks. Infrared spectra were performed on a Bruker Alpha-P Spectrometer. High-resolution mass spectra of tridentate ligands (L1–L5) and Ni(II) complexes (1–5) were obtained by ESI in the positive mode in CH_3CN or CH_3OH solutions using a Micromass Waters® Q-ToF spectrometer. Quantitative gas chromatographic analysis of ethylene oligomerization products was performed on a Varian 3400CX instrument with a Petrocol HD capillary column (methyl silicone, 100 m length, 0.25 mm i.d. and film thickness of 0.5 μm) operating at 36 °C for 15 min followed by heating at 5 °C min^{-1} until 250 °C; cyclohexane was used as the internal standard.

2.2. General oligomerization procedure

Ethylene oligomerization reactions were performed in a 100 mL double-walled stainless Parr reactor equipped with mechanical stirring, internal temperature control and continuous feed of ethylene. The Parr reactor was dried in an oven at 120 °C for 5 h prior to each run, then placed under vacuum for 30 min. A typical reaction was performed by introducing toluene (30 mL) and the proper amount of cocatalyst (MAO or EASC) into the reactor under an ethylene atmosphere. After 20 min, the toluene catalyst solution (10 mL, $[\text{Ni}] =$

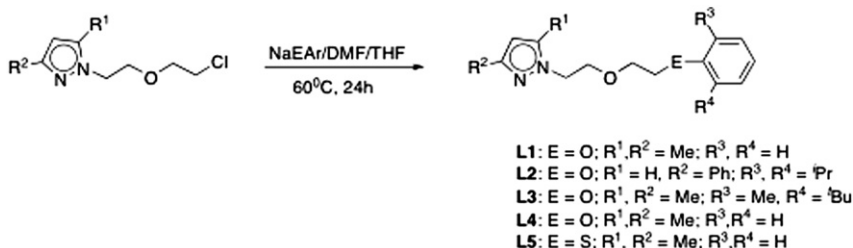
10 μmol) was injected into the reactor under a stream of ethylene and then the reactor was immediately pressurized. Ethylene was continuously fed in order to maintain the desired ethylene pressure. After 20 min, the reaction was stopped by cooling the system to –60 °C and depressurizing. An exact amount of cyclohexane was introduced (as an internal standard) and the mixture was analyzed by quantitative GLC.

3. Results and discussion

The tridentate ether-pyrazol ligands (L1–L5) were prepared by reaction of chloroethoxy-ethyl pyrazole with O- or S-donor aryl groups in DMF/THF in moderate to good yields (41–88%) (Scheme 1). The identity of this class of ligands was established by IR, ESI-HRMS and NMR spectroscopy.

The reaction of (DME) NiCl_2 with 1.1 equiv of the appropriate tridentate ligand (L1–L5) in THF at room temperature afforded the corresponding complexes $[\text{NiCl}_2\text{L}]$ (1–5) (Scheme 2), which were isolated as yellow solids in high yields (typically 81–90%). These nickel complexes show moderate solubility in ethanol or methanol at room temperature. Due to the paramagnetic nature of these compounds, ^1H NMR spectra featured very broad resonances and proved uninformative. The identity of 1–5 was established on the basis of elemental analysis and ESI-HRMS (which indicated the formation of $[\text{M}-\text{Cl}]^+$ ions).

The oligomerization catalytic testing was carried out for each of the nickel precatalysts. The conditions and results of the experiments are reported in Table 1. More details are described in the Experimental Section. When activated with MAO, all catalytic systems proved to be active for dimerization of ethylene with turnover frequencies (TOFs) varying from 19,400 to 35,800 ($\text{mol C}_2\text{H}_4 \cdot (\text{mol Ni}^{-1} \text{h}^{-1})$). As shown in Table 1 (entries 1–4), the ligand environment regarding the substituents on the phenol group influenced the catalytic performance of the nickel precatalysts on ethylene oligomerization, as can be better visualized in Fig. 2. Precatalyst 1, when activated with 250 equiv of MAO, was found to give reasonable activity [$\text{TOF} = 30,900$ ($\text{mol C}_2\text{H}_4 \cdot (\text{mol Ni}^{-1} \text{h}^{-1})$)] along with good selectivity towards 1-butene (65.7%). Increasing the steric hindrance on the pyrazolyl unit by substitution of the methyl group by a phenyl ring at the 3-position (precatalyst 2) caused a decrease in activity by a factor of 1.65. Similarly, the presence of a bulky *tert*-butyl group in the *ortho*-position of the phenol ring (precatalyst 3) also showed lower activity [$\text{TOF} = 20,100$ ($\text{mol C}_2\text{H}_4 \cdot (\text{mol Ni}^{-1} \text{h}^{-1})$)] as compared to the catalytic performance displayed by 1. The abovementioned observations are the direct consequence of the effect of the size of the R substituents toward the insertion of monomers; bulkier substituents offer maximum resistance to monomers coming into the active metal center. On the other hand, the use of a less bulky O-aryl pendant group (precatalyst 4) generated a catalytic system that was more active than that one using complex 1 [$\text{TOF} = 35,800$ ($\text{mol C}_2\text{H}_4 \cdot (\text{mol Ni}^{-1} \text{h}^{-1})$)]. Similar trends have been observed for ethylene oligomerization with MAO-activated nickel complexes bearing tridentate ligands [60,76–78].



Scheme 1. Synthesis of ether-pyrazolyl ligands with pendant O- and S-donor groups.

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