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Spectroscopic and voltametric studies in titanium tris(pyrazolyl)borate catalysts

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Abstract

The ethylene polymerization using $Tp^{Ms*}TiCl_3$ (**1**) ($Tp^{Ms*} = HB(3\text{-mesitylpyrazolyl})_2(5\text{-mesitylpyrazolyl})^-$) and $Tp^{Ms}TiCl_3$ (**2**) ($Tp^{Ms} = HB(3\text{-mesityl-pyrazolyl})_3^-$) was performed in toluene or hexane at 60 °C in the presence of MAO or TiBA/MAO (1:1) as cocatalysts. Higher activities were found for the polymerization reactions carried out in hexane, and using a combination of TiBA/MAO as cocatalysts. Absorciometric measurements in the UV–vis region and cyclic voltammetric have shown that such complexes when activated by MAO were not stable. Measurements carried out in the presence 1-hexene have demonstrated the necessity to add the cocatalyst in the presence of an olefin, i.e., ethylene or hexene-1 in order to stabilize the active species. Furthermore, these studies have revealed that after the activation process most of Ti remains as Ti^{IV}.

Keywords: Titanium; Tris(pyrazolyl)borate; Polymerization; Non-metallocene catalyst

1. Introduction

Polyolefins, such as polyethylene and polypropylene, have increasingly being widely used. Worldwide production volume of polyolefins has grown to more than 80,000,000 tonnes per year and is predicted to rise continuously at a high-rate. Besides the Ziegler–Natta and metallocene catalysts, several generations of non-metallocene compounds have been successfully used in olefin polymerisation [1]. Among them, that one based on Group 4 tris(pyrazolyl)borate ligands has been the subject of intense research activity in our group [2]. In particular, the Ti^{IV} and Zr^{IV} complexes containing sterically hindered Tp′ ligand ($Tp' = HB(3\text{-mesityl-pyrazolyl})_2(5\text{-mesityl-pirazolyl})^-$ (Tp^{Ms*}), $HB(3\text{-mesityl-pyrazolyl})_3^-$ (Tp^{Ms})) have presented comparable activities related to the standard metallocene Cp_2ZrCl_2 [2a,c]. The special features displayed by these catalyst systems prompted us to prepare a set of novel $Tp'MCl_3$ complexes (M = Ti, Zr; $Tp' = HB(3\text{-neopentyl-pyrazolyl})_3^-$ (Tp^{Np}); $HB(3\text{-}tert\text{-butyl-pyrazolyl})_3^-$ (Tp^{tBu}); $HB(3\text{-phenyl-pyrazolyl})_3^-$ (Tp^{Ph}))[2d] in order to investigate if the presence of bulky groups at 3(5) position of the pyrazolyl ring would be a key requirement to design novel high-active catalyst species. However, the very low-activities displayed by them strongly suggest that besides the steric features, others should be driving their catalytic behaviour.

As a part of a continuing effort to understand the effects of the Tp′ ligands with diverse steric properties on the activity we report here some studies on $Tp'TiCl_3$ ($Tp' = Tp^{Ms*}$, Tp^{Ms}, Tp^*) ($Tp^* = HB(3,5\text{-dimethyl-pyrazolyl})_3^-$), using UV–vis spectroscopy, cyclic voltammetry, electrolysis measurements and spectroelectrochemistry. Studies related to the influence of solvent and cocatalyst on the activity for $Tp^{Ms*}TiCl_3$ and $Tp^{Ms}TiCl_3$ are also reported.

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2. Experimental

2.1. Materials

All manipulations were carried out under argon atmosphere using the standard Schlenk tube techniques. Toluene and hexane were dried with Na/benzophenone, distilled and stored under argon. Acetonitrile (Merck, spectroscopic grade) used as solvent in the cyclic voltammetry experiments was dried in molecular sieve and distilled. Tetrabutylammonium tetrafluorborate (Merck) was used without further purification. The catalysts $\mathrm{Tp^{Ms^*}TiCl_3}$ (**1**), $\mathrm{Tp^{Ms}TiCl_3}$ (**2**) and $\mathrm{Tp^*TiCl_3}$ (**3**) were prepared according to the literature [2a]. Ethylene (polymer grade), provided by White Martins Company, and argon were deoxygenated and dried through columns of BTS (BASF) and activated molecular sieves (13 Å) prior to use. MAO (Witco, 5.21 wt.% toluene solution which contains ca. 20 wt.% TMA, trimethylaluminum), TiBA (Akzo, gently supplied by Ipiranga Petroquímica, 8.0 wt.% hexane solution) were used as received.

2.2. Polymerization reactions

Ethylene polymerization experiments were carried out in a 2 L Büchi glass reactor equipped with a magnetic driven mechanical stirrer and temperature measurement indicator. Under argon atmosphere, the suitable amounts of hexane or toluene, and cocatalyst solution were sequentially introduced and then the system was saturated with ethylene. After complete thermal equilibration of the system, the catalyst precursors **1**–**3** were added as solids and the reactor was quickly pressurized (5.2 atm) with stirring. The total volume of the reaction mixtures was 1 L for all polymerizations. The total pressure was kept constant by a continuous feed of ethylene. The polymerization runs were stopped by cooling, degassing the reactor, and introducing 1 mL of methanol. The polymers were washed with acidic ethanol, then ethanol and water, and dried in a vacuum oven at 40 °C for 12 h. On the basis of the results of multiple runs, we estimate the accuracy of these numbers to ±8%.

2.3. Catalyst characterization

UV–vis spectroscopic analyses were performed in a Shimadzu spectrophotometer using an experimental apparatus similar to that described by Coevoet et al. [3]. The cyclic voltammograms (CV) and constant potential electrolysis (coulometry) measurements were taken with a potentiostat/galvanostat (PARC, model 273). All experiments were carried out using a conventional three electrodes cell. Glassy carbon was used as working electrode for CV and platinium gauze for coulometry. An Ag/AgCl electrode was used as the reference electrode and a platinum wire as the auxiliary electrode. Electrochemical data were obtained using 0.1 mol $\mathrm{L^{-1}}$ acetonitrile solutions of tetrabutilammonium tetrafluoroborate as supporting electrolyte. In the cyclic voltammograms, neither anodic nor cathodic peaks were observed in the absence of titanium complexes in the potential range studied. All solutions were deaerated by bubbling high-purity argon. The cocatalyst solutions were prepared with different [Al]/[Ti] molar ratios between 0 and 10 and the cyclic voltammograms were recorded with scan rate of 100 mV $\mathrm{s^{-1}}$. The reported E_f values are the arithmetic mean of E_ap (anodic peak potential) and E_cp (cathodic peak potential) values. The spectroelectrochemical measurements were carried out using a gold mini-grid working electrode, Ag/AgCl as reference and platinum wire as an auxiliary electrode and quartz cell with 0.030 cm optical path. The electronic absorption spectra were recorded using Hewlett Packard Modeles 8453. Successive spectra were record during the redox process of the complexes.

2.4. Polymer characterization

Polymer melting points (T_m) and crystallinities (χ_c) were determined on a Thermal Analysis Instruments DSC-2010 calibrated with Indium, using a heating rate of 10 °C $\mathrm{min^{-1}}$ in the temperature range 40–200 °C. The heating cycle was performed twice, but only the results of the second cycle are reported, since the former is influenced by the mechanical and thermal history of the samples. The intrinsic viscosity was determined in a modified Ostwald capillary viscometer, at 135 °C in decaline, using concentrations of 0.1 g $\mathrm{dL^{-1}}$. Based on the experimental intrinsic viscosity values [η], it was possible to calculate the viscometric molar mass according to the formula $[\eta] = k(\bar{M}_\mathrm{v})^\alpha$ for $k = 6.7 \times 10^{-4}\ \mathrm{dL\,g^{-1}}$ and the $\alpha = 0.67$ [4]. For gel permeation chromatography (GPC) analysis, 2 mg of polyethylene was dissolved in 4 mL of 1,2,4-trichlorobenzene (TCB) in the oven at 180 °C for 1 h. Molar masses and molar mass distributions were investigated with a Waters GPCV 2000 high-temperature GPC instrument, equipped with viscometric detector and four columns (107, 107, 106E, 140). TCB was used as solvent at a flow rate of 1 mL $\mathrm{min^{-1}}$. The analyses were performed at 140 °C. The columns were calibrated with standard narrow molar mass distribution polystyrenes and with linear low-density polyethylenes and polypropylenes.

3. Results and discussion

3.1. Catalyst activity

The ethylene polymerization behavior of **1** and **2** was studied in toluene or hexane at 60 °C using methylaluminoxane (MAO) or a mixture of triisobutylaluminum (TiBA) and MAO (1:1) as cocatalysts. The polymerization results are summarized in Table 1.

The ethylene polymerization results show that both catalyst precursors are highly active under these experimental conditions with the activities varying from 5.4 to 16.6×10^3 kg of PE/mol[Ti]·h. Higher activities were found