

Supported dichlorobis(3-hydroxi-2-methyl-4-pyrone)Ti(IV) catalysts: Evaluation on ethylene polymerization

Paula P. Greco^a, Rodrigo Brambilla^a, Sandra Einloft^a, Fernanda C. Stedile^b,
Griselda. B. Galland^b, João H.Z. dos Santos^b, Nara. R. de S. Basso^{a,*}

^a *Laboratório de Organometálicos e Resinas, Faculdade de Química, PUCRS, Av. Ipiranga 6681, Porto Alegre-90619-900, Brazil*

^b *Laboratório Catalise Ziegler-Natta, Instituto de Química, UFRGS, Av. Bento Gonçalves 9500-Porto Alegre-91570-970, Brazil*

Received 14 January 2005; received in revised form 18 June 2005; accepted 20 June 2005

Available online 27 July 2005

Abstract

Dichlorobis(3-hydroxi-2-methyl-4-pyrone)Ti(IV) complex was grafted on different inorganic supports, namely different kinds of SiO₂, MAO-modified silica, MCM-41, Al₂O₃, ZrO₂ and MgO. The resulting supported catalysts were shown to be active in ethylene polymerization using methylaluminoxane (MAO) as cocatalyst, most of them being even more active than the homogeneous complex. The highest catalyst activities were observed for the Ti complex supported on SiO₂ 948 activated at 450 °C, MCM-41 and Al₂O₃.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Titanium alkoxide; Polyethylene; Polymerization; Supported catalysts; Non-metallocene catalyst

1. Introduction

The production of polyolefins in recent years is continuously growing. Polyolefins are indispensable materials with certain social impact in countless beneficial ways. World-wide production volume of polyolefins has grown to more than 80,000,000 tonnes/year and is predicted to rise continuously at a high rate. Intense research has been carried on olefin polymerization catalysis, in order to develop new catalytic systems capable of producing new materials, as well as developing more economic and versatile processes.

Since the 1980s, metallocene catalysts have become increasingly important for α -olefin polymerization. The metallocene/methylaluminoxane (MAO) system combines high activity with the possibility of tailoring polymer properties [1]. Depending on the metallocene substituent pattern and symmetry, these catalysts permit a strong control of regio- and stereoregularities and of molecular weight distribution of homopolymers, as well as the synthesis of copolymers

with a uniform comonomer distribution. The rapid market penetration of metallocene-based polyethylenes (PE) is due to its high-value attributes, such as greater stiffness and impact strength, greater stretch and puncture resistance and improved sealability. Moreover, polymer properties such as temperature resistance, hardness, impact strength, and transparency can be precisely controlled through the metallocene structure [1].

More recently, new generations of non-metallocene catalysts have been proposed in the literature [2]. The aim is to develop new systems (the so-called *post-metallocene catalysts*), which besides not being covered by patents, are capable to afford further improvements in polymer product properties and production flexibility. While metallocene catalysts are very versatile, the new non-metallocene single-site catalysts provide several advantages, among them their chemical synthesis being much more straightforward in many cases than that of the metallocene. New non-metallocene complexes bearing ancillary ligands such as amido, alkoxo, tris(pyrazolyl)borate, diketimine and related polydentate ligands have appeared as a new trend in this field of research [3–7].

* Corresponding author. Tel.: +55 51 3320 3549; fax: +55 51 3320 3612.
E-mail address: nrbass@pucrs.br (Nara.R. de S. Basso).

Non-metallocene catalysts based on bidentate alcoxide ligands have been proposed in the literature [8–11]. Relatively simple catalytic systems containing alcoxide ligands based on 3-hydroxi-2-methyl-4-pirona have been reported as active for the ethylene polymerization. Sobota and co-workers have synthesized and evaluated the catalysts of the complex diclorobis(3-hydroxi-2-methyl-4-pirona)Ti(IV) in the ethylene polymerization, having shown that this ligand can be used as a good alternative to the cyclopentadienyl ring [12]. Recently, we have synthesized the complex diclorobis(3-hydroxi-2-methyl-4-pirona)Zr(IV) which, in the presence of methylaluminumoxane (MAO) or triisobutylaluminum (TIBA), showed to be active for the ethylene polymerization, producing polymers with high molecular weight. The complex has also revealed to be active when supported on silica or MAO-modified silica [13].

However, these new polymerization catalysts, whether metallocene or non-metallocene, are soluble systems. A solution polymerization process requires separation of the polymer and removal, recovery and purification of the solvent. A gas phase process is lower in cost and energy consumption in comparison with the solution process. As most of the existing polymerization plants run a slurry- and gas-phase process with heterogeneous catalysts, the homogeneous catalysts must be heterogenized on a support in order to apply those processes. In addition the heterogenization of the polymerization catalysts is necessary to avoid reactor fouling with finely dispersed polymer crystals, to prevent excessive swelling of polymers, and to produce polymer particles of a desired regular morphology.

Many routes for the preparation of supported metallocenes have been reported in the literature [14,15]. Silica, chemically-modified or not, is the most employed support. Nevertheless, other supports such as modified montmorillonite [16], diamond black powder [17], sulfated metal oxides [18], MCM-41 (Mobil Composition of Matter) [19] or polymers [20,21] have also been investigated. These procedures afford different catalysts which, in turn, produce polyolefins with different properties.

In the present work we investigated the catalytic activity of the complex diclorobis(3-hidroxi-2-methyl-4-pirona)Ti(IV) grafted on different inorganic carriers, namely SiO₂, MAO-modified silica, MCM-41, MgO, Al₂O₃ and ZrO₂. The choice of these supports is based on the fact that they present different textures (surface area and pore diameter), as well as surface sites bearing different acid/base characteristics.

The resulting systems were evaluated in ethylene polymerization, having methylaluminumoxane (MAO) as cocatalyst.

2. Experimental

2.1. General procedures

All the experiments were performed under inert atmosphere using the Schlenk technique. Toluene was dried by

usual methods existing on literature and stored under dried argon. The titanium complex was synthesized accordingly to the literature [12].

The supports were activated under vacuum ($P < 10^{-4}$ mbar) for 16 h. The activation temperature for SiO₂ 2133 (PQ Corporation, surface area: 350 m² g⁻¹; pore diameter: 272 Å), SiO₂ 956 (Grace, surface area: 350 m² g⁻¹; pore diameter: 272 Å) and ZrO₂ (Riedel, surface area: 20 m² g⁻¹) was 110 °C, for SiO₂ 948 (Grace, surface area: 255 m² g⁻¹; pore diameter: 248 Å) was 110° and 450 °C, while MCM-41 (surface area: 1,100 m² g⁻¹), MgO (Riedel, surface area: 60 m² g⁻¹) and Al₂O₃ (Inlab, surface area: 110 m² g⁻¹) the activation temperature was 450 °C. These activated supports were stored under argon atmosphere. MAO-supported silica (SMAO, 23 wt.% Al, Witco) was used without treatment. MCM-41 was synthesized according to the literature [22]. MAO (10.0 wt.% toluene solution) was purchased from Witco.

2.2. Preparation of supported catalysts

The supported catalysts were prepared by the grafting method. In a typical experiment, for instance, an initial toluene solution of the synthesized titanium complex [dichlorobis(3-hidroxi-2-methyl-4-pirone)titanium(IV)] corresponding to 0.5 wt.% Ti/support was added to the pretreated support (1.0 g) and the resulting slurry was stirred for 1 h at 80 °C, and then filtered through a fritted disk. The resulting solids were washed with 15 aliquots (2.0 cm³) of toluene and dried under vacuum for 4 h.

2.3. Characterization of supported catalysts

Titanium loadings on different supports were determined by X-ray fluorescence spectroscopy (XRF) using a Rigaku (RIX 3100) wavelength dispersive XRF spectrometer tube operated at 50 kV and 70 mA, bearing a LiF 200 crystal and a scintillation counter. Samples were pressed as homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems.

Specific surface area was determined by the BET method from N₂ adsorption data at 77 K using a Gemini 2375 (Micrometrics). The samples were outgassed at 333 K for 6 h before measuring the nitrogen adsorption.

The catalyst morphology was identified through scanning electron microscopy (SEM), using a JEOL JSM 5800 equipment. The catalysts were fixed on a carbon tape and then coated with gold by conventional sputtering techniques.

2.4. Polymerization reactions

Ethylene homopolymerizations were performed using a 0.3 dm³ of toluene or hexane in a Pyrex glass reactor connected to a constant temperature circulator, with an internal temperature indicator, equipped with mechanical stirring and inlets for argon and the monomer. MAO was used as co-

Download English Version:

<https://daneshyari.com/en/article/9614445>

Download Persian Version:

<https://daneshyari.com/article/9614445>

[Daneshyari.com](https://daneshyari.com)