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Journal of Molecular Catalysis A: Chemical 260 (2006) 135–143
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Immobilization and activation of 2,6-bis(imino)pyridyl Fe, Cr and V precatalysts using a $MgCl_2/AlR_n(OEt)_{3-n}$ support: Effects on polyethylene molecular weight and molecular weight distribution

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Received 24 April 2006; received in revised form 13 June 2006; accepted 12 July 2006
Available online 22 August 2006

Abstract

Ethylene polymerizations carried out with various bis(imino)pyridyl iron, chromium and vanadium complexes immobilized on a $MgCl_2/AlR_n(OEt)_{3-n}$ support gave relatively broad polyethylene molecular weight distributions in the case of iron, but high molecular weight and a very narrow molecular weight distribution with vanadium, indicative of a single active species. The narrow MWD was confirmed by melt rheometry. Similar results were obtained after reaction of the bis(imino)pyridyl complex $LVCl_3$ (**6**) with MeLi or $AlEt_3$, where alkylation of the pyridine ring gives a complex $L'VCl_2$ (**7**). In the case of chromium, a bimodal distribution was obtained, with evidence of incomplete catalyst immobilization. The polyethylene molecular weights obtained with the iron complexes were strongly dependent on the substituents in the bis(imino)pyridyl ligand, and were somewhat higher than have been obtained in homogeneous polymerization. In contrast, the molecular weights obtained with the bis(imino)pyridyl chromium and vanadium complexes were much higher that those previously obtained under homogeneous conditions. In all cases, the activities of the immobilized catalysts were higher than those found in homogeneous polymerization.

Keywords: Catalysis; Ethylene; Immobilization; Magnesium chloride; Polymerization

1. Introduction

Bis(imino)pyridyl iron complexes of type $\{2,6\text{-}[ArN{=}C(Me)]_2C_5H_3N\}FeCl_2$ have been shown to be very active precatalysts for ethylene polymerization [1,2]. However, in contrast to the great majority of homogeneous olefin precatalysts, these systems typically give polyethylene with relatively broad molecular weight distribution. In many cases a bimodal molecular weight distribution is obtained and evidence has been presented that, for systems activated with methylaluminoxane (MAO), this is caused by the formation of a low molecular weight fraction resulting from chain transfer to aluminium, particularly in the early stages of polymerization [3]. The question remains as to whether chain transfer to aluminium is the only reason for the broad polydispersities obtained with these systems, or whether more than one type of active species is operative [4]. Strong evidence for the presence of different active species has recently been provided by Barabanov et al. [5], who used ^{14}CO radiotagging to determine the numbers of active centres and propagation rate constants in homogeneous polymerization. The results obtained indicated the presence of highly reactive but unstable active centres producing a low molecular weight polymer fraction, as well as less active but more stable species producing higher molecular weight polymer. Iron-based precatalysts can be activated by both MAO and aluminium trialkyls and it has been reported that narrow molecular weight distribution can be obtained using $Al\textit{i}Bu_3$ [6,7] or $\textit{i}Bu_2AlOAl\textit{i}Bu_2$ [8]. Following these studies, carried out under homogeneous polymerization conditions, several groups investigated the immobilization and activation of bis(imino)pyridyl iron precatalysts on various supports, including silica [9–11] and magnesium chloride [12,13]. The $MgCl_2$-supported systems consistently gave broad polyethylene molecular weight distribution, irrespective of the type of aluminium trialkyl used as cocatalyst.

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1381-1169/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2006.07.030

Recently, we and others have investigated the immobilization of a range of early- and late-transition metal precatalysts using supports of type $MgCl_2/AlR_n(OR)_{3-n}$, prepared by reaction of AlR_3 with either solid, spherical adducts of $MgCl_2$ and ethanol [12,14] or adducts of $MgCl_2$ and 2-ethylhexanol in hydrocarbon solution [15]. Widespread implementation of homogeneous and single-site catalysts in polyolefin production, especially in gas-phase and slurry processes, is dependent on the development of effective techniques for catalyst immobilization and considerable research is being carried out in this field [16]. Our own studies have concentrated on the use of supports typically prepared by the reaction of $AlEt_3$ with spherical, partially dealcoholated adducts of $MgCl_2$ and EtOH [17]. The spherical particle morphology of the support is retained and replicated during catalyst immobilization and polymerization, leading to the formation of spherical polymer particles without reactor fouling.

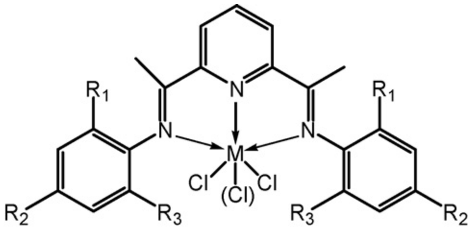
In the present work, we have investigated the immobilization and activation of different bis(imino)pyridyl iron(II) precatalysts, including the effect of cocatalyst type and concentration. In order to assess whether with these systems the polyethylene polydispersity is dependent on the transition metal, the ligand or the metal/ligand combination, bis(imino)pyridyl chromium(II) and vanadium(III) precatalysts have also been immobilized and activated using the same $MgCl_2/AlR_n(OEt)_{3-n}$ support.

2. Experimental

2.1. Materials

All manipulations were performed under an argon atmosphere using glove box (Braun MB-150 G1 or LM-130) and Schlenk techniques. Light petroleum (b.p. 40–60 °C) and dichloromethane were passed over a column containing Al_2O_3 and stored over 4 Å molecular sieves. All the solvents were freeze-thaw degassed at least twice prior to use.

Precatalysts **1**–**4** (structures shown in Scheme 1) were prepared according to various literature procedures [3,18,19]. $\{2,6\text{-}[ArN{=}C(Me)]_2C_5H_3N\}CrCl_2$ (**5**; Ar = 2,6-di*iso*propylphenyl) and $\{2,6\text{-}[ArN{=}C(Me)]_2C_5H_3N\}VCl_3$ (**6**; Ar = 2,6-di*iso*propylphenyl) were prepared following procedures similar to those described by Devore et al. [20] and by Gambarotta and coworkers [21]. $\{2,6\text{-}[ArN{=}C(Me)]_2(2\text{-}MeC_5H_3N)\}VCl_2$ (**7**; Ar = 2,6-di*iso*propylphenyl) was prepared by the reaction of **6** with MeLi in toluene as described by Gambarotta and coworkers [21]; after solvent removal under vacuum, the residue was redissolved in ether and after filtration the ether was removed under vacuum to yield a dark green solid.



Cat.	M	R_1	R_2	R_3
1	Fe	Me	Me	Me
2	Fe	*i*Pr	H	*i*Pr
3	Fe	Cl	Me	Me
4	Fe	Me	H	H
5	Cr	*i*Pr	H	*i*Pr
6	V	*i*Pr	H	*i*Pr

Scheme 1. Structure of bis(imino)pyridyl metal (Fe, Cr and V) precatalysts.

$AlEt_3$ (25 wt.% solution in toluene) and $ZnEt_2$ (1.0 M solution in hexane) were purchased from Aldrich. Al*i*Bu_3 (1 M solution in hexane) and MAO (25 wt.% solution in toluene) were purchased from Fluka and Akzo Nobel, respectively.

Ethylene (3.5 grade supplied by Air Liquide) was purified by passing over columns of 4 Å molecular sieves and BTS copper catalyst.

2.2. Support preparation and catalyst immobilization

Support preparation was performed by the addition of $AlEt_3$ to a slurry of an adduct $MgCl_2{\cdot}1.1EtOH$ (average particle size d_{50} 82 μm) in light petroleum ($AlEt_3/EtOH = 2$) at 0 °C, after which the mixture was kept at room temperature for 2 days with occasional agitation. The resultant support was washed with light petroleum three times and dried under argon flow and subsequently under vacuum until free flowing. The Al contents of the support were determined by the H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. The ethoxide content in $MgCl_2/AlEt_n(OEt)_{3-n}$ support was determined by gas chromatography (GC) analysis of the ethanol content of a solution obtained by dissolving 100 mg of support in 5 mL of BuOH containing a known quantity of PrOH as an internal standard. The Al and OEt contents of the support were 3.89 and 4.89 wt.%, respectively, indicating an overall support composition $MgCl_2{\cdot}0.17AlEt_{2.25}(OEt)_{0.75}$.

Catalyst immobilization was effected by mixing the support (50–100 mg) with a precatalyst solution in dichloromethane (2 mL, containing 0.5–1.0 μmol of precatalyst) and keeping at room temperature overnight. The slurry of the immobilized catalyst in dichloromethane was diluted with light petroleum and used directly in ethylene polymerization.

2.3. Polymerization procedure

Polymerization was carried out in a 1 L Premex autoclave by charging the immobilized catalyst (50–100 mg, containing 0.5–1.0 μmol precatalyst), slurried in approximately 100 mL light petroleum, to 400 mL light petroleum containing the desired amount of cocatalyst, at 50 °C and an ethylene pressure of 5 bar. After catalyst injection, polymerization was continued at constant pressure for 1 h and with a stirring rate of around 1000 rpm. After venting the reactor, 20 mL of acidified ethanol were added and stirring was continued for 30 min. The polymer was recovered by filtration, washed with water and ethanol and dried in vacuo overnight at 60 °C.

2.4. Polymer characterization

Molecular weights and molecular weight distributions of the resulting polymers were determined by means of gel perme-