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ScienceDirect
Applied Catalysis A: General 325 (2007) 87–90
APPLIED CATALYSIS A: GENERAL
www.elsevier.com/locate/apcata

Effect of alkylaluminum cocatalyst on ethylene polymerization with nickel-α-diimine complex

Caroline G. de Souza, Roberto F. de Souza, Katia Bernardo-Gusmão *

Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, P.O. Box 15003, CEP 91501-970 Porto Alegre, Brazil

Received 14 November 2006; received in revised form 9 March 2007; accepted 12 March 2007
Available online 15 March 2007

Abstract

Ethylene polymerization was carried out with two nickel(II)(α-diimine) complexes: 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine-dichloro-nickel(II) (**1**) and 1,4-bis(2,6-diisopropylphenyl)-ethanediimine-dichloronickel(II) (**2**) combined with alkylaluminum activators like methylalumoxane (MAO), trimethylaluminum (TMA), and ethylaluminum sesquichloride (EASC). The activity of these systems and the proprieties of the polymeric materials are strongly influenced by the choice of the ligand structure and, more dramatically, by the nature of the cocatalyst. EASC has been shown as giving higher productivities than TMA or MAO with both complexes, attaining 3966 kg PE/(mol Ni·h). Complex **2** gives lower productivities but produced polymers with higher polymer melting points (T_m) and crystallinity than catalyst **1**.

Keywords: Polymerization; Nickel; Diimine; Ethylene

1. Introduction

Considerable academic and industrial efforts have been devoted to the study of nickel-α-diimine complexes, which have become very popular since the precursor work of Brookhart and co-workers. Much research on variations of the ligand structures used to perform the tailoring has been published. Numerous papers have been devoted to studying the effects of reaction parameters on the ethylene polymerization reaction. This number becomes yet larger if one includes studies of heterogeneised catalysts conducted by several research groups.

There is agreement about the nature of the activity of these particular complexes on polymerization. The blocking of the axial positions around the nickel core prevents β-elimination reactions and this consequently gives rise to continuous insertion process polymerization [1,2].

Still, very few papers have questioned the convenience of using methylalumoxane (MAO) as a cocatalyst, considering the possibility of its replacement by other less expensive organoaluminum compounds [3]. Our studies have shown that MAO is not necessary to activate nickel–halogen complexes, as might be expected judging from classic nickel chemistry reports. This knowledge opens new possibilities for improvement of already recognized as important nickel-α-diimine complexes as catalysts for the production of branched polyethylene [4,5].

We describe herein a systematic study of the effect of the nature of cocatalyst on the catalytic performance of two selected nickel-α-diimine complexes.

2. Experimental

2.1. Materials and characterisation

All experiments were performed under an atmosphere of dry argon using standard Schlenk tube techniques. The complexes were prepared and purified according to literature procedures. Solids were dried under reduced pressure and toluene was distilled under argon from sodium/benzophenone immediately prior to use. MAO was purchased from Witco and used without further purification. Trimethylaluminum (TMA) and ethylaluminum sesquichloride (EASC) were purchased from Akzo Nobel and were used with previous dilution.

Polymer melting points (T_m) and crystallinities (χ_c) were determined with a Thermal Analysis Instruments DSC-2010.

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* Corresponding author. Tel.: +55 51 33166318; fax: +55 51 33167304.
E-mail addresses: caroline.guterres@ufrgs.br (C.G. de Souza), rfds@iq.ufrgs.br (R.F. de Souza), katiabg@iq.ufrgs.br (K. Bernardo-Gusmão).

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doi:10.1016/j.apcata.2007.03.007

Polymer samples were heated in open pans from 40 to 180 °C, held at this temperature for 5 min, cooled to −20 °C and then heated again to 180 °C. The heating and cooling rate was 10 °C/min. The analyses were performed under nitrogen. Melting point temperatures and degree of crystallinity were determined in the second scan.

NMR analyses were performed by the Centro Petroquímico de Pesquisa e Desenvolvimento (CEPPED)–ULBRA. The polymer microstructure was qualitatively and quantitatively analyzed by ^{13}C NMR spectroscopy. The branches were classified as methyl, ethyl, propyl, butyl, pentyl and hexyl+ (hexyl and longer) in accordance with previous work [6]. The spectra were obtained with a varian mercury 400 MHz spectrometer operating at 100.6 MHz, at 130 °C, with a 74° flip angle, an acquisition time of 1.5 s and a delay of 5.0 s. Sample solutions of the polymer were prepared in tetrachloroethane deutered in a 5 mm tube.

2.2. Polymerization reactions

Ethylene polymerization reactions were performed in a 450 mL Parr stainless steel autoclave equipped with magnetically driven mechanical stirring, thermocouple and pressure gauge. The reaction temperature was controlled by a thermostatic circulation bath with a serpentine inside the reaction vessel. A typical reaction run was performed by introducing 2 mmol of the desired alkylaluminum cocatalyst and 10 μmol of the nickel(II) complex in 100 mL of toluene saturated with ethylene. The ethylene pressure was raised to 14 atm and continuously fed. After 30 min, the reactor was depressured and the polymer was precipitated in acidified ethanol, filtered, washed and dried for 48 h at 60 °C under reduced pressure.

3. Results and discussion

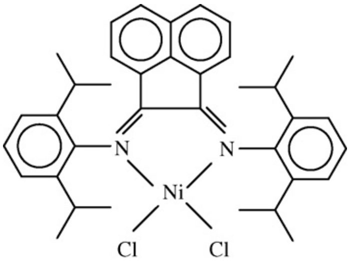
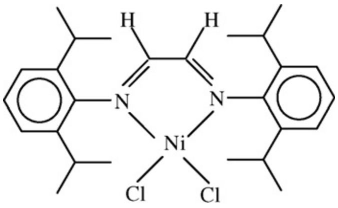
Complexes **1** and **2** were tested in ethylene polymerization at 14 atm, 30 °C, with a reaction time of 30 min using toluene as solvent. The cocatalysts used were methylaluminoxane (MAO), trimethylaluminum (TMA) or ethylaluminum sesquichloride (EASC). These were introduced to the reactor in amounts calculated to obtain an aluminum to nickel molar ratio (Al/Ni) of 200. Under these reaction conditions, complexes **1** and **2** are active in ethylene polymerization, with productivities between 280 and 3966 kg of ethylene converted per mole of nickel, per hour, corresponding to turnover frequencies (TOFs) varying from 2.8 to 39 s^{-1}, as described in Table 1.

Table 1 shows that the performance of the system depends on the combination of catalyst and cocatalyst, the highest catalytic activity being observed with **1** activated by EASC (entry 3).

Complex **1** shows higher productivities than **2**, independent of the cocatalyst used. Both catalysts were more active when combined with MAO than with TMA (entries 1, 2, 4, 5) and even more active in the presence of EASC (entries 3, 6). This behavior of complexes **1** and **2** has been previously observed when combined with MMAO [7].

The most relevant effects are those of the cocatalysts, insofar as the replacement of MAO by less expensive cocatalysts has been extremely sought after. Rausch and co-workers have described the activity of Ni-α-diimine complexes combined with different cocatalysts. They demonstrated that DEAC (diethylaluminum chloride) and DCDAO (1,3-dichloro-1,3-diisobutyldialuminoxane) are more active than MAO, TMA, and TIBA (triisobutylaluminum) [3]. The results shown in Table 1 are in agreement with these results and introduce EASC, an even better cocatalyst. This better productivity of the

Table 1
Ethylene polymerization with complexes nickel α-diimines

Entry	Complexes	Alkylalluminum	m (g)	Productivity (kg PE/(mol Ni·h))	TOF[a] (s^{-1})	T_m[b] (°C)	χ_c[b,c] (%)
1		TMA	8.0	1600	16	102	20
2		MAO	14.7	2932	29	<20	<6
3		EASC	19.8	3966	39	76	<6
4		TMA	1.4	280	2.8	135	57
5		MAO	1.7	340	3.4	133	44
6		EASC	2.4	480	4.8	129	38

Reaction conditions: ethylene pressure = 14 atm, 10 μmol of nickel, Al/Ni = 200, 100 mL of toluene, 30 °C, 30 min.

[a] TOF: turnover frequency = mol ethylene converted per mol of Ni per second.

[b] T_m measured by DSC.

[c] Crystallinity calculated using the enthalpy of fusion of a perfectly crystalline polyethylene (293 J/g).