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Distinct behaviour of Ti and Hf supported catalysts in the polymerization of different monoalkenes

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$MgCl_2$ supported Ti and Hf catalysts were comparatively tested with respect to the polymerization of differently shaped monoalkenes. The ratio between the average polymerization rates of Ti and Hf catalysts during the first 120 min (V_p^{Ti}/V_p^{Hf}) is 10 for ethylene, increases to 63 for propylene and returns to ~12–20 for higher or bulkier monoalkenes, suggesting a distinct shape selectivity of active sites.

(Keywords: Ziegler-Natta polymerization; monoalkenes; hafnium catalyst; titanium catalyst; shape selectivity)

Introduction

Previous investigations pointed out the importance of evaluating the role played by Ti and Hf catalytic sites in bimetallic catalysts for the production of different ethylene polymers (*HDPE* to *LLDPE*), the density of which was modulated by copolymerization with 1-alkenes[1]. In this connection, the polymerization of monoalkenes having different structures and steric hindrance is now reported in the presence of catalysts containing either Ti or Hf as the sole transition metal component. The monomer structure affects the average rates of homo- and copolymerization for the two systems in a substantially different way, thus suggesting that Hf sites have distinct shape selectivity with respect to Ti sites. Such a result can be of interest for modulating polymer properties by bimetallic catalysts.

Experimental

Commercial grade $Al(i\text{-}C_4H_9)_3$, $Ti(O\text{-}n\text{-}C_4H_9)_4$, $HfCl_4$, polymerization grade ethylene, propylene and 1-butene were used without further purification.

Commercial grade 1-hexene, 4-methyl-1-pentene (4MP) and 1-octene were purified by refluxing over metallic sodium followed by distillation. Research grade n-heptane (Fluka) was purified according to the usual procedure.

Magnesium-supported Hf and Ti catalysts were prepared according to procedures similar to those previously described[2].

Ethylene[1] and propylene[3] polymerization were carried out as previously described at 50°C and 4×10^5 Pa.

Homopolymerization experiments of 1-butene, 1-hexene, 1-octene and 4MP were carried out in n-heptane at 50°C in a magnetically stirred schlenk vessel.

Copolymerization experiments were carried out at 25°C under the same experimental conditions. All runs were stopped with acidified methanol and the coagulated polymer was dried under vacuum.

N.m.r. spectra were recorded by a Varian Gemini 200 spectrometer in 5 mm tubes by using 10% (w/v) solutions in 1,2,4-trichlorobenzene at 110°C. ^1H n.m.r. spectra were recorded at 200 MHz. Spectral conditions were as follows: size, 11968 points; spectral width, 3 kHz; pulse, 30°; acquisition time, 2 s; number of scans, 1. ^{13}C n.m.r. spectra were recorded at 50.3 MHz under conditions of full proton decoupling. Spectral conditions were as follows: size, 23936 points; spectral width, 15 kHz; pulse, 70°; relaxation delay, 2 s; acquisition time, 0.8 s; number of scans, 20000. No weighing function was applied before the Fourier transformation.

I.r. spectra were recorded on polymer films by a Perkin-Elmer 1600 Fourier transform i.r. spectrophotometer. Viscosity measurements were carried out in tetrahydronaphthalene at 135°C by a Desreaux-Bischoff dilution viscometer.

Results and discussion

The supported transition metal catalysts used in the present work were prepared by precipitation from paraffin solution of the respective tetra-n-butanolate with alkylaluminium chlorides in the presence of spray-dried magnesium dichloride. The starting mixture composition was selected in order to obtain a 1/1 molar ratio between magnesium and the transition metal in the final catalyst[2]. These catalysts were activated by addition of triisobutylaluminium with the molar ratio ($AlR_3/Ti = 10–500$ and $AlR_3/Hf = 10–100$, the highest values being used for ethylene) granting the maximum activity for each polymerization experiment.

These catalysts were used in the polymerization of ethylene, of linear α-olefins with increasing side chain length (propylene, 1-butene, 1-hexene and 1-octene) and of a branched 1-olefin, 4MP. The polymerization of each monomer was carried out under the same experimental

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Table 1 Comparison between Ti and Hf based catalysts in the homopolymerization of ethylene and α-olefins[a]

	Catalyst Ti/Mg				Catalyst Hf/Mg				
		IF (%)[c]		$[\eta]$[d]		IF (%)[c]		$[\eta]$[d]	
Monomer	V_p[b]	N.m.r.	Ext.	(dl g^{-1})	V_p[b]	N.m.r.	Ext.	(dl g^{-1})	V_p^{Ti}/V_p^{Hf}
Ethylene	3 579 000	–	–	26.7	357 300	–	–	57.2	10.0
Propylene	27 360	62	19	2.8	432	73	46	10.3	63.0
1-Butene	3778	83	38	2.2	219	91	75	5.5	17.2
1-Hexene	7780	83	–[e]	3.4	689	90	–[e]	9.8	11.3
1-Octene	7750	91	–[e]	3.4	657	93	–[e]	8.4	11.8
4-Methyl-1-pentene	3740	90	67	5.0	180	95	90	16.8	20.8

[a] In n-heptane at 50°C in the presence of $Al(i\text{-}C_4H_9)_3$

[b] After 120 min, expressed as moles of monomer/(moles of transition metal × h)

[c] IF, isotactic fraction, evaluated either by ^{13}C n.m.r. or as per cent fraction insoluble (Ext.) in n-heptane (polypropylene) or in diethyl ether [poly(1-butene) and poly(4-methyl-1-pentene)]

[d] In decahydronaphthalene at 135°C

[e] Totally soluble in both diethyl ether and n-heptane

Table 2 Average rates of polymerization (productivity ratios) of different monoalkenes (MA) with respect to 4-methyl-1-pentene (4MP) in homopolymerization[a] and copolymerization[b] experiments, in the presence of Hf or Ti catalysts

	Homopolymer		Copolymer			
	V_p^{MA}/V_p^{4MP}[c]		4MP (%)[d]		$V_{cop}^{MA}/V_{cop}^{4MP}$[e]	
Monomer	Ti	Hf	Ti	Hf	Ti	Hf
Ethylene	957	1985	0.8	1.9	124	52
Propylene	7.3	2.4	18	25	4.6	3.0
1-Butene	1.0	1.2	37	37	1.7	1.7
1-Hexene	2.1	3.8	35	34	1.8	1.9

[a] Runs carried out at 25°C

[b] Runs carried out at 50°C

[c] Productivity ratio after 120 min for different monoalkenes referred to 4MP

[d] Mole per cent of 4MP units in the copolymer, evaluated by ^{13}C n.m.r.

[e] Ratio of the average homo- and cross-polymerization rates after 120 min

conditions both in the presence of Ti and Hf catalysts. Ethylene and propylene polymerization were carried out at constant pressure, while for the other monomer the variation of concentration was limited by keeping conversion below 25%. Catalyst performances were evaluated by determining polymer productivity, expressed as the average polymerization rate after 120 min [V_p: moles of monomer/(moles of transition metal × h)]. As shown previously during kinetic investigations of ethylene[1,2] and 1-olefins polymerization[2,3] in the presence of similar catalysts, after 120 min the process has reached steady conditions (V_p constant). Moreover, intrinsic viscosity and, whenever possible, stereoregularity of the polymers were also determined.

As expected from previous investigations[1,3] Ti/Mg catalysts show a higher activity than Hf/Mg systems, while the latter give higher molecular weight polymers. For both systems the productivity decreases from ethylene to propylene, while some distinctive differences occur in going to bulkier olefins. The general trend of decreasing activity with increasing steric hindrance around the double bond[4] is substantially confirmed for both metals. The modest increase of productivity when going from 1-butene to longer homologues (1-hexene or 1-octene) can be associated with the actual lower concentration of the first monomer due to its higher volatility without substantial variation of the steric hindrance. In any case this increase is within the limits of experimental accuracy and is a common feature of the two transition metals (*Table 1*).

In the case of Ti, however, the productivity drops markedly from propylene to higher homologues, whereas in the case of Hf the productivity remains of the same order of magnitude. The different shape selectivity of the two metals is well evidenced by the 'productivity ratio' evaluated for the different monomers (V_p^{Ti}/V_p^{Hf} in *Table 1*). According to the above experimental observations, this ratio shows a much higher value for propylene with respect to both ethylene and 1-olefins with more than four carbon atoms. Smaller but significant differences between Ti and Hf can be observed also for the other monomers; in particular the comparison of V_p for 1-hexene and 4MP indicates that Hf catalysts are more sensitive to chain branching. This result can be used for interpreting some difference in the sequence distribution of 1-hexene/4MP copolymers obtained in the presence of the two catalytic systems[5].

During the homopolymerization, the 'productivity ratio' for different monoalkenes with respect to 4MP is different when using Hf or Ti catalysts (*Table 2*). The same trend is observed at least qualitatively for the values of productivity ratios during the copolymerization. On this basis the above data can help to predict the probability of block formation and in general sequence distribution in the copolymerization with the different catalysts. The incorporation of the two monomers in copolymer macromolecules is also dependent on the rates of cross-propagation reactions, which can modify the values of V_p^{MA}/V_p^{4MP} ratios. Accordingly, in copolymerization experiments of each monomer with 4MP, at low conversion (<25%) the ratios of the incorporation rates ($V_{cop} = V_{homo} + V_{cross}$) are different from those of the homopolymerization (*Table 2*) but show the same trend.

Due to the difficulty to account for the influence of the many parameters involved, a detailed quantitative evaluation is not possible. The present results clearly show that Hf and Ti catalysts can produce copolymer macromolecules with different compositions and sequence distribution starting from the same comonomer mixture (*Table 3*).

Table 3 Structural characterization of the copolymerization products from equimolar amounts of 4-methyl-1-pentene (4MP) with different monoalkenes (MA)

Comonomer	Catalyst	Polymer		
		4MP[a] (mol%)	l_{4MP}[a,b]	l_{MA}[a,b]
Ethylene	Ti/Mg	0.8	1.0	~100
Ethylene	Hf/Mg	1.9	1.0	~50
Propylene	Ti/Mg	18	1.6	8.2
Propylene	Hf/Mg	25	1.9	6.2
1-Butene	Ti/Mg	37	1.9	3.2
1-Butene	Hf/Mg	37	2.0	3.4
1-Hexene	Hf/Mg	34	1.8	3.4
1-Hexene	Ti/Mg	35	2.1	3.5

[a] Evaluated by ^{13}C n.m.r.
[b] Average sequence length

The stereoregularity of propylene, 1-butene, 1-hexene and 4MP polymers, determined whenever possible by both solvent extraction and ^{13}C n.m.r. (*Table 1*), confirms the presence of different sites in the 1-alkene polymerization using the two catalysts. Different valence states of the transition metal, different steric requisites of the site and the unequal distribution of sites having different acidic character[6], can also be considered. The different isotacticity values determined by the two techniques can be explained by considering that the Hf catalyst mainly contains sites giving rise to high molecular weight isotactic chains, whereas non-stereospecific sites yield lower molecular weight molecules. On the other hand, the Ti catalysts contain a wider family of sites, including those giving lower molecular weight but good isotacticity. These aspects deserve further work before a definite explanation can be provided.

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