

Olefin polymerization using supported metallocene catalysts: development of high activity catalysts for use in slurry and gas phase ethylene polymerizations

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Abstract

Reaction of hydroxylated silica and alumina supports with methyl aluminoxane in toluene suspension provides chemically modified supports suitable for use in slurry and gas-phase polymerizations of ethylene or propylene on treatment with a variety of metallocene dichloride complexes. In particular, aluminas derived from calcination of sol–gel precursors feature high degrees of surface hydroxylation in comparison with commercially available silica (or even alumina) of similar surface area and total porosity. This feature provides a mechanism for increasing the amount of aluminoxane on the former supports, such that commercially acceptable productivities (> 10 kg PE/g support \times h) are observed at relatively low, total levels of aluminoxane or other alkylaluminum compounds in slurry or gas-phase polymerizations, respectively. A variety of evidence indicates that leaching of active catalyst from these alumina supports occurs to a minor extent under slurry conditions, particularly at higher temperatures in the presence of additional aluminoxane. At lower temperatures, this does not occur to an appreciable extent but the morphology and bulk density of the polymer formed is unsuitable for use in a gas-phase process. This can be attributed to the method for synthesis of the sol–gel alumina precursor which results in irregular particles with a broad particle size distribution. Copolymerization of ethylene with 1-octene or 1-hexene results in formation of linear, low density, PE with a narrow composition distribution as revealed by temperature rising elution fractionation. These studies indicate that less comonomer is incorporated using these supported metallocene catalysts than their soluble analogues under otherwise identical conditions. Finally, some of the resins prepared under slurry conditions (and to a lesser extent in a gas-phase process), exhibit properties consistent with the presence of low levels of long-chain branching; this feature appears to be reasonably general for a variety of simple metallocene complexes. © 1998 Elsevier Science B.V.

1. Introduction

It is widely anticipated that metallocene complexes of the group IV elements in combination

with aluminoxane or single, component co-catalysts will supplant traditional Z–N catalysts in commercial polymerization processes. Attractive features of these catalysts include high intrinsic activity based on the transition metal, facile control over polymer MW and MWD, uniform incorporation of co-monomer and con-

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trol of polymer stereoregularity; indeed a number of poly(olefin) producers have already commenced production of these resins using supported versions of these catalysts [1].

Most of the commercial applications emphasize the superior properties of the polymer obtained; barriers to commercialization for the production of commodity thermoplastics include low activity with respect to co-catalyst and the support, leaving high levels of ash content in the final product at commercially acceptable rates of productivity, as well as difficulties encountered in melt-processing of some of these resins.

The latter phenomenon can be largely alleviated through the use of constrained geometry catalysts in a solution process [2,3]. Under these conditions, HDPE, and, to a greater extent, LLDPE with a narrow MWD and containing low levels of long-chain branching is produced; the latter phenomenon leads to LLDPE resins with vastly improved, melt-processability because of improved melt-strength through formation of entanglements. It has been claimed that the level of branching can be controlled, is process dependent, and requires a constrained geometry catalyst system, presumably so as to allow competitive co-polymerization of ethylene with long-chain oligomers with terminal unsaturation¹.

In this paper, we summarize the results of extensive studies concerning the utility of various approaches to supported catalyst systems in both slurry and gas-phase processes. In particular, supported systems based on alumina offer the promise of much higher productivities at relatively low co-catalyst loadings. In addition, we demonstrate that incorporation of long chain branching into LLDPE and to a lesser extent HDPE is possible using a supported catalyst in a slurry or, to a lesser extent, gas-phase process

using conventional metallocene complexes. This latter finding does not seem to be widely appreciated².

2. Development of supported catalysts

Earlier work involving propylene polymerization using silica and alumina supports and metallocene catalysts had revealed that partially, hydroxylated supports, when treated with alkylaluminum compounds (e.g. AlMe_3), were suitable for the preparation of supported metallocene catalysts in the presence of methylaluminoxane co-catalyst [8]. At about this time, a more useful approach in terms of overall productivity was reported [9], which involved treatment of hydroxylated silica with aluminoxane, followed by the metallocene complex; this approach forms the basis for numerous patents and patent applications in this field³.

Interestingly, in our earlier work, the activity of alumina based systems was comparable to that of silica based systems despite having lower surface area and total porosity [8]. This suggested that use of alumina based supports might offer considerable advantage, in terms of productivity, over silica. Relatively high surface area aluminas are available commercially, while very high surface area and total porosity aluminas are available by calcination of super-critically dried boehmite⁴, produced by sol-gel hydrolysis of aluminum alkoxide precursors⁵.

We decided to investigate the latter approach as a method for obtaining aluminas of comparable porosity to readily available silicas (many of

¹ For mathematical simulations of long-chain branching in poly-olefins see Ref. [4]. For mechanistic work on this process see Ref. [5].

² Reported in part at Worldwide Metallocene Conference, Metcon'95 sponsored by Catalyst Consultants, Houston, TX, May 1995. The same phenomenon has been noted using polymer-supported, metallocene catalysts in a gas-phase process [6,7].

³ Selected patents: see e.g. Refs. [10–13]. Publications: for a lead reference to the literature see Ref. [14].

⁴ For applications of super-critically dried alumina precursors, see e.g. Ref. [15].

⁵ For a lead reference to sol-gel alumina chemistry see Ref. [16].

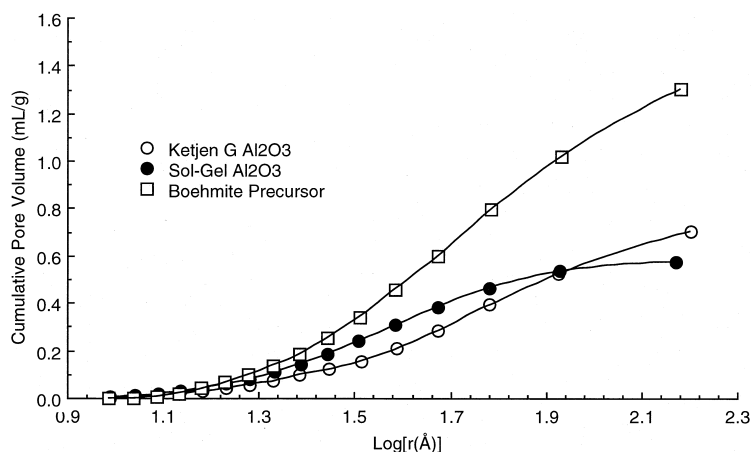


Fig. 1. Cumulative porosity (ml/g) vs. \ln [pore radius (\AA)] for Ψ -boehmite and γ -alumina along with comparison data for Ketjen Grade G alumina (BET data summarized in Table 1).

which are produced by the same approach). Having said that, control of particle morphology and size distribution is an important feature for successful use in gas-phase (or slurry) polymerization processes; this technology is well-developed in the case of silica but not in the case of alumina derived from sol-gel precursors.

Hydrolysis of $\text{Al}(\text{O}^i\text{Bu})_3$ using the conditions developed by Klein et al. [17], provides access to high surface area Ψ -boehmite (ca. 400–500 m^2/g), which can be calcined under a variety of conditions to provide, poorly crystalline, γ - Al_2O_3 , as revealed by powder X-ray diffraction⁶. During this process, collapse of large pores ($r > 100 \text{\AA}$, Fig. 1) is observed so that total surface area and porosity decreases significantly (to ca. 250–350 m^2/g and 0.4–0.8 ml/g, respectively), although the pore-size distribution becomes noticeably narrower on calcination.

Following calcination, fully hydroxylated alumina was obtained by passage of water-saturated helium over the surface at 300°C [18]. Related approaches were used for the preparation of partially hydroxylated silica (Davison

655 or PQ silica) and a commercially available alumina (Ketjen, Grade G) of similar total porosity and surface area⁷.

The hydroxyl content of these supports was estimated by titration with AlMe_3 as described earlier [8], and typical data are summarized in Table 1 for a variety of alumina and silica based supports. As can be seen from these results, alumina based supports feature much higher levels of surface hydroxylation than silica, and the effect is particularly pronounced for the sol-gel derived material.

This feature can obviously be exploited using the approach described earlier [9–14]. Reaction of these hydroxylated supports with methylaluminumoxane in toluene suspension at 25°C, followed by thorough washing of these materials, provides the chemically modified supports, whose properties are summarized in Table 2. Based on both weight gain, recovered aluminoxane, and in certain cases, methane evolved it is clear that significant quantities of aluminoxane can be deposited on the alumina supports, compared with silica, and the effect is particularly dramatic in the case of the sol-gel derived alumina, the chemically treated support being about 2/3 by weight aluminoxane.

⁶ Data available from the authors on request. We thank Professor Linda F. Nazar of the Department of Chemistry, University of Waterloo for access to this equipment.

⁷ For dehydroxylation of silicas and aluminas see Ref. [19].

Table 1
Properties of supports used

Entry	Support	Code	S.A. ^a (m ² /g)	P.V. ^b (ml/g)	P.R. ^c (Å)	mol OH ^d /mol support
1	Davisil-645	DS	300	1.15	75	0.064
2	PQ silica	PQ	440	3.10	144	0.075
3	Dispal 18N4	DN	150	0.43	58	0.230
4	Ketjen G	KG	345	0.90	52	0.370
5	sol-gel alumina	SG	300 ± 50 ^e	0.6 ± 0.2 ^e	50 ± 5 ^e	0.50 ± 0.05 ^e

^aSurface area as measured by BET.

^bCumulative adsorption pore volume for pores < 400 Å.

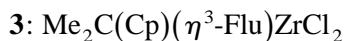
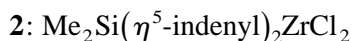
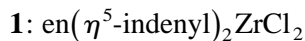
^cAverage pore radius.

^dSurface hydroxylation as measured by titration with trimethylaluminum.

^eAverage values for different samples.

Having said that the stoichiometry of reaction between alumina and aluminoxane compared with silica and this material is considerably different (as might be expected); considerably more aluminoxane can be deposited on silica, based on surface OH concentration — the limiting factor with silica is the lower total degree of surface hydroxylation possible ⁸.

These chemically treated supports were then contacted with various metallocene complexes (**1**–**3**) in toluene solution at 25°C; following filtration and washing, the amount of metallocene remaining in the filtrate was estimated using UV-visible spectroscopy on treatment of the filtrate with a solution of anhydrous HCl in toluene [8]. This data is summarized in Table 2 for metallocene **1**; significant quantities of various common metallocene complexes can be deposited on these supports, and again the alumina-based supports incorporate significantly higher total levels of a given metallocene complex compared with silica.



The surface Al:Zr ratio (ca. 20–25:1) for all of these supports is reasonably similar at maxi-

mal loadings of both MAO and metallocene. This illustrates, to a first approximation, that surface–catalyst interactions are dominated by chemistry between aluminoxane and metallocene and are only indirectly influenced by the support material itself. The physiochemical state of both the adsorbed aluminoxane and metallocene complex is of obvious interest; all of these supported catalysts were obtained as yellow to red, free-flowing solids and future work will focus on these important issues ⁹.

3. Screening of supported catalysts in propylene polymerization

Based on work reported earlier [8–14], it was expected that these supported catalysts should behave in a manner similar to that of their soluble counterparts if the support chemistry leads to ‘single-site’ catalysts. This feature was borne out by conducting propylene polymerization using both **1**/SG/MAO and **3**/SG/MAO. These polymerizations were conducted in the presence of additional aluminoxane (total Al:Zr = 1000:1); at lower loadings of aluminoxane (< 200:1) or on substitution of aluminoxane by other alkylaluminum compounds, productivities

⁸ Fully hydroxylated silica has a surface OH coverage corresponding to 0.12 mol OH/mol support [20]. This corresponds to a maximal loading of ca. 20 mmol MAO/g support.

⁹ The interaction of metallocene complexes with both inorganic oxide supports and with aluminoxanes has been studied by a variety of techniques. There appears to have been less work conducted on the hybrid materials reported here. For lead references see Refs. [21–23]. See also a review in Ref. [24] for recent developments in aluminoxane chemistry.

Table 2
Adsorption of MAO and metallocene **1** on supports

Entry	Support ^a	mmol OH ^b /g oxide	mmol MAO ^c /g oxide	Al:OH	mmol Zr ^d /g oxide	Al:Zr	Code ^e
1	DS	1.07	11.7	10.9	0.39	27.9	1/DS/MAO
2	PQ	1.25	13.8	11.0	0.43	25.6	1/PQ/MAO
3	DN	2.26	13.8	6.11	0.59	23.3	1/DN/MAO
4	KG	3.63	21.4	5.89	0.98	21.8	1/KG/MAO
5	SG	4.90	29.0	5.91	1.50	19.3	1/SG/MAO

^aFor descriptions of the supports, see Table 1.

^bDetermined by titration with AlMe₃.

^cBased on final weight and also from recovered MAO.

^dMaximum loadings determined from residual catalyst in solution.

^eMAO-modified support designation.

were much lower in these slurry polymerizations.

In the case of **1**/SG/MAO or **2**/SG/MAO, isotactic poly(propylene) was formed with a microstructure consistent with that produced by its soluble counterpart under similar conditions (Table 3). Syndiotactic PP was produced using the supported version of **3**, in contrast to recent work where the formation of isotactic material has been observed [25].

The only differences observed in using the supported vs. soluble catalysts was the slightly lower MW of the polymer obtained in some cases using the supported catalyst, while the catalytic activity of the supported metallocene catalysts was about 1/3 that of their soluble

counterparts under identical conditions. Since the propagation rate is significantly lower (i.e. by a factor of 3), and the MW (which is proportional to R_p/R_{tr}) of the polymer is largely unaffected using a supported catalyst, this suggests that R_{tr} must decrease by at least the same magnitude as R_p — i.e. chain transfer reactions are intrinsically slower using a supported metallocene catalyst.

Some authors have attributed this effect to a reduction in bimetallic, chain-terminating reactions on supporting the metallocene [26]; alternatively, the observation that dimers of cationic and neutral alkyl metallocene complexes appear to have lower propagation rates (which would indirectly decrease polymer MW) under slurry conditions [27], provides an alternative explanation for the effects observed on supporting metallocene complexes. While a recent report suggests that supported catalysts of this type studied here are not ‘site-isolated’ and a method for doing so is disclosed [28] (for details of the MWD of these polymers see Ref. [29]), based on the broad MWD and the much lower productivities observed, there is reason to question whether intact metallocene complexes are involved¹⁰.

Table 3
Propylene polymerization using supported and soluble metallocene catalysts

Catalyst ^a	Al:Zr ^b	A ₁ ^c	A ₂ ^d	M_n (K) ^e	M_w/M_n ^e	% mmmm ^f
1/SG/MAO	1100:1	9.24	5.17	9.72	2.11	82.4
1/PQ/MAO	1100:1	2.68	2.22	9.91	2.29	81.2
1/MAO	2000:1	38.0	n/a	15.9	1.85	81.3
2/SG/MAO	1100:1	15.24	7.62	27.9	1.91	87.2
2/MAO	2000:1	43.6	n/a	21.4	1.94	83.7
3/SG/MAO	2000:1	4.2	1.0	44.8	1.60	81.8 ^g
3/MAO	2000:1	13.8	n/a	48.7	1.75	86.2 ^g

^aFor catalyst/support designations, see Table 1Table 2; conditions: toluene 500 ml; C₃H₆ 45 psig; 40°C.

^bTotal aluminoxane to Zr ratio.

^c10³ kg PP/mol Zr × h.

^dkg PP/g support × h.

^eDetermined by SEC.

^fDetermined by ¹³C NMR spectroscopy.

^g% rrrr for catalyst **3**.

¹⁰We note the reaction of hydroxylated SiO₂ with e.g. **1** even under mild conditions (25°C, 1–2 h), results in formation of bis(indenyl)ethane, suggesting partial, hydrolytic decomposition of **1** [8]; surface-bound Zr species in which one indenyl ring was still intact would still be chiral and could produce e.g. isotactic poly(propylene). For further evidence indicating formation of different sites, see Ref. [30].

4. Ethylene polymerization using supported metallocene catalysts

Ethylene polymerization using some of the supported catalyst systems was investigated in toluene suspension at 25°C and in hexane suspension at 75°C in the presence of MAO and modified MAO (Akzo MMAO-3A), respectively; relevant data are summarized in Table 4. While there is little difference between the silica and alumina based supports in terms of productivity based on metallocene complex, the productivity based on the amount of support employed is obviously higher with the alumina based systems because of their higher total metallocene (and aluminoxane) content. Under commercially applicable conditions (Table 4, entries 8–12), the activity based on Zr is only about 1/3–1/2 that of the soluble catalyst and the productivity based on the amount of support (and to a lesser extent, total MAO) is usefully high (> 20 kg PE/g support h).

A number of experiments were performed to illustrate the heterogeneity of these catalysts in toluene suspension. Contact of the support

1/SG/MAO with MAO (Al:Zr ca. 1000:1), followed by filtration and washing, gave rise to soluble and insoluble fractions; the former was inactive for ethylene polymerization — i.e. < 100 mg PE after 1 h (unless additional catalyst **1** was deliberately added, indicating that significant quantities of MAO were still present in the soluble portion) while the insoluble fraction, when resuspended in toluene containing MAO showed the same activity as summarized in Table 4. Moreover, exposure of 1/SG/MAO to MAO and ethylene for ca. 10 min followed by filtration, washing and drying led to PE-encapsulated catalyst and a soluble filtrate. The former was active for ethylene polymerization when re-exposed to the polymerization conditions while the latter was inactive in the absence of additional metallocene catalyst.

Having said that, at higher temperatures in hexane suspension, some reactor fouling was observed during polymerization. This may be due to either some leaching of metallocene complex from the support at elevated temperatures or agglomeration of primary polymer particles due to higher productivity rates compared with conventional, supported catalysts.

SEM studies revealed that at low coverages of PE (ca. 10–20% by weight), polymer particles of irregular shape and a broad size distribution were produced in toluene suspension using the alumina-based, supports (which more or less mirrored the properties of the supports themselves)¹¹. The bulk density of these polymers (ca. 0.1–0.2 g/cm³) was generally quite low and may be reflective of both the primary particle properties as well as the high aluminoxane content of the chemically treated supports.

Thus, these studies demonstrate that acceptable levels of productivity are possible using supported metallocene catalysts based on alumina, however particle morphology and size

Table 4

Ethylene polymerization using supported catalysts^a

Entry	Catalyst ^b	Zr (μmol)	A ₁ ^c	A ₂ ^d	M _w (K)	M _w / M _n
1	1/DS/MAO	5.6	8.9	2.2	197	2.9
2	1/PQ/MAO	5.6	5.1	1.4	150	3.0
3	1/DN/MAO	4.0	5.6	2.9	132	2.4
4	1/KG/MAO	6.0	5.4	5.2	150	2.3
5	1/KG/MAO	6.0	5.5	5.5	138	2.3
6	1/SG/MAO	6.1	8.9	12.7	168	2.4
7	1/SG/MAO	6.1	7.1	10.1	188	2.5
8	1 ^e	2.0	400.0	n.a.	111	2.4
9	1/SG/MAO ^c	2.0	114.0	65.4	97	2.3
10	1/SG/MAO ^e	2.0 ^f	68.0	39.0	93	2.3
11	1/SG/MAO ^g	2.0 ^g	65.0	32.5	116	2.4
12	1/SG/MAO ^c	2.0 ^h	50.0	25.0	98	2.1

^aConditions: toluene (0.5 l), 20°C, C₂H₄ 60 psig, Al:Zr 1000:1 except where noted.

^bFor catalysts see Table 2.

^cActivity in 10³ kg PE/mol Zr × h.

^dActivity in kg PE/g support × h.

^eConditions: hexane (1.3 l), 75°C, 60 psig C₂H₄, 1 h.

^fAl:Zr = 860:1.

^gAl:Zr = 640:1.

^hAl:Zr = 320:1.

¹¹ We thank D. Weber of the Department of Biology, University of Waterloo for assistance with the SEM measurements, data available from the authors on request.

Table 5
Copolymerization of ethylene and 1-octene or 1-hexene with soluble and supported catalysts^a

Entry	Support	C ₂ H ₄ ^b	t (min)	A ₁ ^c	M _w (K)	M _w /M _n	M ₂ ^d	m ₂ ^e
1	none	15	30	10.0	333	2.3	0.0	0.0
2	none	15	10	11.3			57.4	11.2
3	none	15	30	17.2			80.2	25.2
4	none	15	10	19.2			80.2	29.6
5	none	30	10	14.7	111	2.4	40.3	5.2
6	none	30	10	36.6			66.9	17.6
7	none	30	30	23.5			66.9	15.7
8	none	45	10	10.4			31.0	2.8
9	none	45	10	41.7	60	2.4	57.4	11.8
10	SG/MAO	60	30	8.0	190	2.8	0.0	0.0
12	SG/MAO	15	30	9.9			80.2	18.9
13	SG/MAO	30	30	13.3	72	2.0	66.9	10.3
14	SG/MAO	45	30	16.4	73	2.1	57.4	9.4
15	SG/MAO ^f	60	60	65.0	116	2.4	0.0	0.0
16	SG/MAO ^f	60	60	144.0	76	2.0	n.d.	2.6

^aConditions: 0.5 l of toluene, Zr = 5.54 μmol, Al:Zr 630:1, 20°C except where noted; data are for metallocene 1.

^bEthylene pressure (psig).

^cActivity in 10³ kg PE/mol Zr × h.

^dMol% 1-octene or 1-hexene in initial feed.

^eMol% 1-octene or 1-hexene in the copolymer as determined by ¹³C NMR spectroscopy.

^fConditions: hexane 1.3 l, [Zr] = 2.0 mM, Al:Zr 640:1, 75°C, 15.0 ml 1-hexene.

distribution are unsuitable for use in e.g. gas-phase processes.

5. Copolymerization of ethylene and α-olefins

Copolymerization of ethylene and 1-octene in toluene suspension at 25°C, and of ethylene and 1-hexene in hexane suspension at 75°C were studied, using some of these supported catalysts, and the data are summarized in Table 5. Comonomer content was estimated from the ¹³C NMR spectrum of the polymers, using established procedures [31]. A comparison of the data obtained using supported vs. soluble catalysts reveals that somewhat less comonomer is incorporated with the former compared with the latter, at identical feed ratios. This finding is consistent with small diffusional resistances to co-monomer migration to the supported metallocene complex and/or modified reactivity of the complex on the support towards co-monomer. At higher temperatures, in hexane suspension, no attempt was made to limit conversion

and at a given feed ratio, these supported catalysts incorporate significantly higher levels of 1-hexene compared to classical Z–N catalysts under the same conditions.

One finding that was observed under both sets of conditions, was that the productivity of these catalysts was significantly higher in the presence of comonomer; this effect, which has been noted before [32], may be physical, or alternatively, aluminoxane/metallocene interactions that lead to (reversible) formation of less active species [25]¹², may be lessened as a result of competitive binding/incorporation of comonomer. Another feature was that polymer MW was reduced in the presence of co-monomer, despite the significantly higher productivities; this suggests facile chain transfer to the metal (or to co-monomer) by e.g. β-H-elimination. Future work will focus on this issue.

¹² Alkylaluminum-stabilized, cationic metallocene complexes have been reported; although more robust, these species are not as active as in olefin polymerization, see e.g. Ref. [33].

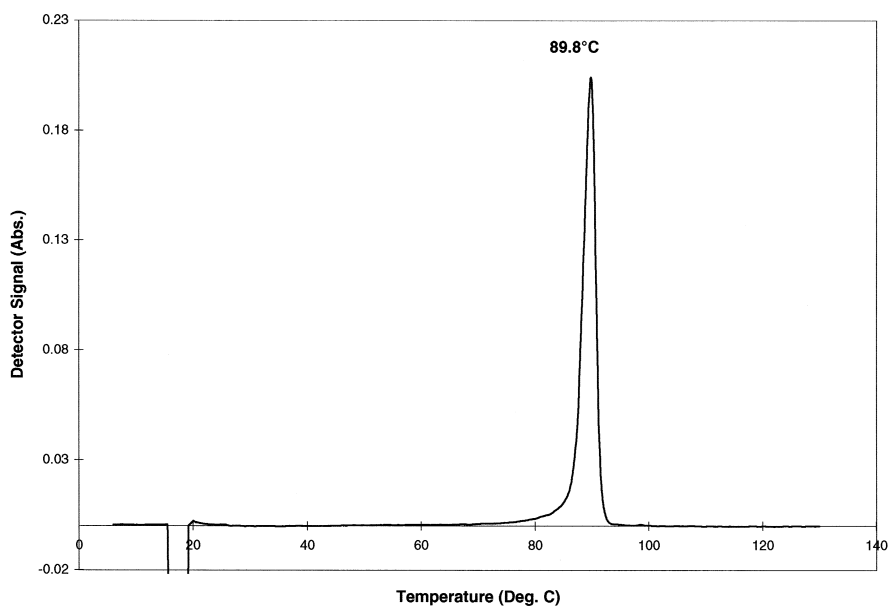


Fig. 2. Crystallizability distribution for a 1-hexene, ethylene co-polymer (5.3 mol% 1-hexene) prepared using **1**/PQ/MAO in hexane slurry (85°C, 200 psig C₂H₄) in the presence of MMAO-3A (Al:Zr 1000:1).

Some of the 1-hexene copolymers produced were analyzed by temperature rising elution fractionation (TREF). Unlike conventional LLDPE, these resins have extremely narrow, unimodal crystallizability distributions (e.g. Fig. 2), consistent with a homogeneous composition distribution. This, in combination with the narrow MWDs observed, is convincing evidence for the ‘single-site’ nature of these supported catalysts. An important implication of these findings, is that LLDPE copolymers produced using supported metallocene catalysts, require far lower levels of co-monomer incorporation to obtain a given density of material; this should allow for production of specialty LLDPE resins (e.g. ULLDPE) at low total levels of co-monomer.

6. Gas-phase polymerization of ethylene using supported metallocene catalysts

A limited number of runs involving ethylene polymerization or ethylene/1-hexene copoly-

merization were conducted using these supported catalysts in a continuous, semi-pilot scale, gas-phase reactor. Based on the work under slurry conditions, using the alumina based catalysts, considerable problems with reactor fouling were anticipated and in fact, observed. It was difficult to maintain continuous operation for this reason, but initial productivities under commercially applicable conditions were promising (> 10 kg/g). Further work focused on the use of silica-based catalysts, which were less susceptible to this problem and will be described elsewhere [34].

Some of the resins produced using these supported catalysts showed significant shear thinning, as revealed by melt viscosity measurements. Additional work, involving capillary, melt viscosity measurements, revealed that this phenomenon was also observed in resins prepared under slurry conditions in hexane at elevated temperatures and even in toluene suspension at lower temperatures [35]. This melt behaviour is consistent with the presence of long-chain branching (LCB) in these polymers. This

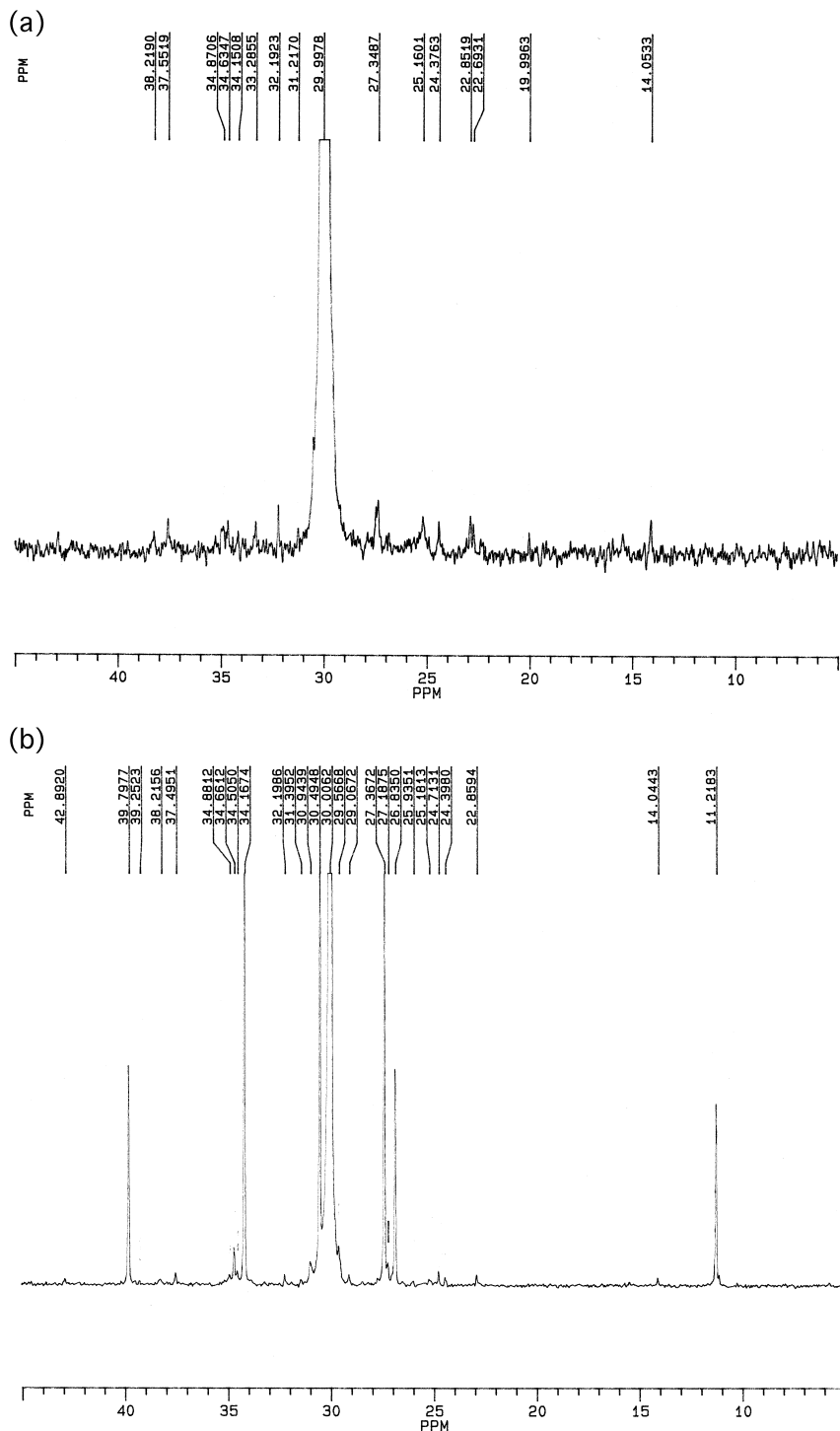


Fig. 3. (a) ^{13}C NMR spectrum of ethylene homopolymer prepared using **1**/PQ/MAO in the gas phase (90°C , 200 psig C_2H_4) in the presence of TIBAL (Al:Zr 200:1); LCB = 0.4 br/1000C. (b) ^{13}C NMR spectrum of 1-butene, ethylene copolymer (9.0 mol% 1-butene) prepared using **1**/PQ/MAO in the gas phase (90°C , 200 psig C_2H_4) in the presence of TIBAL (Al:Zr 200:1); LCB = 0.5 br/1000C.

Table 6
Long-chain branching in ethylene homo- and copolymers

Catalyst	Conditions (<i>T</i> , solvent, <i>C</i> ₂)	Co-catalyst (Al:Zr)	Comonomer (mol% in PE)	LCB (br/1000 C)
1/PQ/MAO	85°C, hexane, 200 psig	MMAO-3A (1000:1)	1-hexene (5.3)	0.6 ± 0.05
1/PQ/MAO	85°C, hexane, 200 psig	MMAO-3A (1000:1)	none	0.4
1/PQ/MAO	90°C, none, 200 psig	TIBAL (200:1)	1-butene (9.0)	0.5
1/PQ/MAO	90°C, none, 200 psig	TIBAL (200:1)	none	0.4

was subsequently verified by ¹³C NMR analysis of both HDPE (Fig. 3(a)) and LLDPE (Fig. 3(b)) prepared using the same supported catalyst under similar conditions which revealed a diagnostic signal at δ 32.2 ppm that is associated with branches longer than six carbon atoms [31]. Also, in the homopolymer and in a 1-butene copolymer, a weak signal at 42.8 ppm, due to the presence of a methine carbon arising from LCB was evident.

Some data concerning the level of LCB as a function of polymerization conditions is outlined in Table 6. As a general feature, the incidence of LCB was higher in copolymerization than in homopolymerization, and LCB incorporation was also higher under slurry conditions than in gas-phase. The highest levels observed (ca. 0.6 branches/1000 carbons), are comparable to those claimed in a solution process at much higher temperatures using a constrained geometry catalyst. Moreover, the occurrence of LCB was essentially independent of the metallocene complex supported, although the levels of LCB were dependent on catalyst structure.

These findings are significant — it has been implied, mainly in the patent literature [2,3], that use of a constrained geometry catalyst is 'required' to obtain PE with LCB, whereas the present results suggest that this phenomenon is much more general than had been previously appreciated [6,7]. While, to our knowledge, the mechanism for LCB formation has not been conclusively determined [4,5], the most reasonable explanation involves co-polymerization of unsaturated oligomers. This makes a great deal

of sense in a solution process, but seems much less likely in a slurry or gas-phase process; the observation that it does occur and relatively efficiently at that, suggests that oligomeric chains, produced by e.g. β-H-elimination, encounter significant diffusional resistances to migration away from the active sites of these supported catalysts; this in turn may be related to the significantly improved productivity of these systems compared with earlier approaches to supported catalysts. Alternatively, the mechanism for branch formation in these systems may not involve copolymerization of unsaturated oligomers¹³.

7. Conclusions

In summary, we have developed supported catalysts that combine high productivity with formation of polymers and copolymers with narrow MW and composition distributions, that can be used in both slurry and gas-phase processes. Although the alumina based systems are the most active on a per support basis, problems with particle morphology (and/or high production rates) mitigate against their use in conventional gas-phase reactors at present. The observation of LCB in many of the resins prepared suggest that modifications to improve the per-

¹³ Other possibilities could include chain isomerization via repetitive β-H elimination/insertion processes and/or remote C–H activation processes, see e.g. [36,37].

formance of these systems are worthwhile and are under active investigation.

8. Experimental section

All synthetic work was conducted under N₂ atmosphere using Schlenk techniques and reagent grade solvents that were dried/deoxygenated and distilled under nitrogen according to established methods [38]. All organic reagents were received from commercial sources and purified as required prior to use [39]. Methyl aluminoxane (PMAO) and modified methyl aluminoxane (MMAO-3A) were obtained from Akzo Chemicals; the former was concentrated in vacuo to dryness (10⁻³ mmHg) to provide solid MAO for subsequent use. Zirconocene complexes **1–3** were prepared by literature methods¹⁴, and purified by recrystallization from toluene prior to use. Davison 655 silica was purchased from Aldrich Chemical while PQ silica (Grade 3010, Quantum Chemical) and Ketjen G alumina (Akzo Chemicals) were donated by Novachem Chemicals. Aluminum tri-*sec*-butoxide was distilled under vacuum and stored under nitrogen prior to hydrolysis. Toluene for polymerizations (Fisher Chemicals, Optima Grade) was dried/deoxygenated by reflux and distillation from Na and benzophenone under N₂; it was stored over activated MS 4 Å under nitrogen prior to use. Propylene and ethylene (C.P. grade) were purchased from Matheson Gas and purified by passage through a 1 l mixed bed catalyst consisting of BASF-R311 and MS 4 Å (1:2 w:w). 1-octene was purified by distillation from Na metal and 1-hexene and hexane were purified by passage through beds of Roche A-2 alumina and Q-5 catalyst under nitrogen.

¹⁴ Complex **1**: Ref. [40]. Complex **2**: Ref. [41]. Complex **3**: Ref. [42]. The procedure reported was modified by extracting the crude product with dichloromethane (to remove LiCl) followed by recrystallization from toluene.

9. Polymerization procedure

A 1–2 l pressure vessel was charged with solvent (0.5–1.0 l), co-monomer, if desired, and additional MAO (or MMAO-3A) and the solution was then saturated with monomer at the required temperature and pressure with stirring (500–1500 rpm). Solutions or slurries of catalysts in solvent were introduced via a small sample cylinder (25 ml capacity) by over-pressurizing with nitrogen prior to introduction into the reactor. Monomer was supplied on demand and consumption was measured by calibrated mass-flow meters. Polymerizations were quenched by the addition of a solution of ethanol in a small volume of solvent via the sample cylinder. The reactor was then vented and cooled to RT prior to discharging the contents through a drain valve or following disassembly. Polymer was filtered off and washed with methanol, or solvent was removed in vacuo prior to precipitation of the polymer using methanol. Polymer was de-ashed using a solution of 3.0 M HCl in MeOH in a blender, followed by washing with methanol and drying in vacuo at 60°C and 10⁻³ mm Hg.

10. Polymer characterization

¹³C NMR and ¹H NMR spectra of polymers prepared were acquired on a Bruker AC-300 spectrometer in 1,2,4-TCB and 1,1,2,2-tetrachloroethane-*d*₂ solution at 125–140°C, respectively. Chemical shifts were referenced with respect to added benzene-*d*₆ (ca. 10% v:v) and residual protonated solvent, respectively. Quantitative ¹³C NMR spectra of LLDPE were acquired with inverse-gated decoupling, a 90° pulse width, 10 s relaxation delay, a 200 ppm sweep width and 32 K data points. Typically 10,000 transients were averaged.

SEC analyses were conducted on a Waters 150C chromatograph on a Jordi mixed-bed column (10–10³ K), and equipped with DRI, Vis-

cotek differential viscometer and Milton-Roy KMX-6 LALLS detectors at 145°C in 1,2,4-TCB solution. Samples were eluted at a flow rate of 1.0 ml/min and columns and detectors were calibrated using both a broad MWD PE and narrow MWD polystyrene standards.

DSC analyses were conducted on a Perkin-Elmer DSC-2 Model calibrated using indium metal. A sweep rate of 20°/min from 25–200°C was employed, the sample was then cooled to 25°C at 10°C/min and the second trace recorded using the same heating program.

TREF analyses were conducted on a system constructed in-house. Silica columns were equilibrated in 1,2,4-TCB and the polymer, dissolved in TCB was loaded onto the columns at 130°C. The column was cooled to 20°C at a rate of 1°C/h and after several hours at 20°C, the polymer was eluted by raising the temperature to 130°C at a rate of 10°C/h. Polymer concentration was determined using a fixed wavelength IR detector tuned to the C–H stretching frequency of methylene groups (2920 cm⁻¹) while short chain branching frequency and distribution were determined using a second IR detector tuned to the stretching frequency of methyl groups (2960 cm⁻¹); deconvolution, as described in detail elsewhere [43], was necessary to correct for peak overlap and the IR response, expressed in terms of branches/1000 C atoms, was calibrated using linear hydrocarbons of known composition.

11. Preparation of sol–gel alumina [17]

A solution of water (13.5 ml, 0.75 mol) in HLPC grade ⁱPrOH (500 ml) was heated to 80°C under nitrogen. Aluminum tri-*sec*-butoxide (61.5 g, 0.25 mol) was added with vigorous stirring over a period of 15–20 min. The mixture was kept at 80°C for 1–2 h, cooled to room temperature and filtered, washed with ⁱPrOH, and dried in vacuo at 80°C and 10⁻³ mm Hg to provide boehmite precursor (12–13 g).

5 g quantities of this material were placed inside a quartz tube inside a horizontal tube furnace. The material was heated under a stream of helium to 500–600°C and kept at this temperature for 1 h. Oxygen was then passed over the surface for another hour at this temperature and then the furnace was cooled to 300°C under a flow of helium. Water-saturated helium was then passed over the surface for 12 h at 300°C to fully hydroxylate the alumina.

12. Adsorption of MAO on alumina

1 g of fully hydroxylated alumina (ca. 10 mmol OH groups) was slurried in 100 ml of dry toluene. A solution of MAO in 50 ml of toluene (2.05 g, 35 mmol) was added slowly via cannula at room temperature over a period of 15–20 min. Vigorous methane evolution was observed and could be measured by connecting a gas buret, containing toluene presaturated with methane to the flask; the amount evolved was generally 75–80% of the theoretical amount of surface hydroxyl groups present, as measured by titration with AlMe₃ [8]. After stirring at room temperature for 3–4 h, the mixture was filtered under nitrogen, washing repetitively with dry toluene until the filtrate, when dried in vacuo at 10⁻³ mm Hg, achieved constant weight.

13. Adsorption of metallocene 1 on MAO-modified alumina

A slurry of MAO-modified alumina (2.6 g, ca. 29 mmol of MAO) in toluene (100 ml) was prepared under nitrogen at room temperature. A solution of complex 1 (250 mg, 0.60 mmol) in hot toluene (100 ml) was prepared under nitrogen and this was rapidly added to the modified support. The mixture was stirred at room temperature for 3–4 h and then filtered under nitrogen. The orange solid was washed with toluene until the filtrate was colorless. The filtrate was then treated with a solution of anhydrous HCl in

toluene to convert any alkylated material back to the dichloride, diluted to volume in a 500 ml volumetric flask and residual complex **1** analyzed by UV-visible spectroscopy as described earlier [8]. Selected samples were submitted for neutron activation analysis for Zr and the results were in agreement with those determined by the method outlined here.

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