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Ethylene (co)polymerization with supported-metallocenes prepared by the sol–gel method

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Abstract

Four supported metallocenes prepared by the sol–gel method were tested by ethylene homopolymerization and in ethylene/1-hexene copolymerization. The effects of Al/Zr ratio, polymerization temperature and cocatalysts were evaluated. Catalyst A2, produced by TEA and MAO treatments showed the highest activity (180×10^3 kg PE/mol Zr h^{-1}) among the tested systems at Al/Zr = 1000. A2 showed thermal stability on polymerization performed at a temperature as high as 120°C. All the systems exhibited activity in the presence of common alkylaluminum (TMA, TEA, TIBA). Comonomer effect was observed in the copolymerization of ethylene with 1-hexene, where the comonomer incorporation is about 7 mol%. SAXS measurements of the employed xerogel suggested a weakly branched polymeric texture. Metal content in the resulting polymers showed extremely low levels of Zr. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Zirconocene; Silica-supported metallocenes; Ethylene polymerization

1. Introduction

Metallocene catalysts activated by methylaluminoxane (MAO) display high activity and productivity of polymers with a narrow molecular weight distribution, high comonomer incorporation and homogeneous comonomer distribution in the polymeric chain. Advances in metallocene catalyst chemistry now provide novel routes for the manufacture of a large variety of different polyolefins materials [1–4].

Nevertheless, these soluble catalysts are unsuitable for industrial applications, where heterogeneous catalyst systems are required for gas phase and slurry polymerization processes or for large-scale polymer production. One approach to overcome this problem is the heterogeneization of such catalysts, by supporting them on carriers. Several routes, employing different supports, are described in the scientific and patent literature [5–8].

Methods of supporting aluminoxane-activated zirconocene catalysts can be generally classified in three groups: immobilization of MAO on the support prior to zirconocene grafting; direct zirconocene immobilization and pre-contacting of aluminoxane and metal complex in solution before supporting. In all three cases, MAO leaches a part of the supported zirconocene to the solution. Chemically tethered zirconocenes has been prepared aiming at preventing the catalyst leaching from the surface during polymerization. Whether the catalyst is actually desorbed from the support during the polymerization process is not totally clear [8].

In most of the cases a drastic reduction in catalyst activity partially due to a small quantity of metallocene on the support has been observed. The loading of the catalyst is low and limited by the external surface of the silica. In other words, the reaction is dependent on the reactivity and availability of surface OH groups and leaving out the ligands from the metallocene. Moreover, bulk ligands (such as cyclopentadienyl, indenyl) from the complexes avoid the further reaction of molecules with the remaining silanol groups [9]. In fact, it is attributed that only ca. 1% of the supported species is effectively active for polymerization [10].

Another reason for such small catalyst activity might be caused by the silica surface itself, which plays the role of a steric hindrance ligand around the active site. From such a point-of-view, the modification of the support with organosilane compounds playing the role of spacers prior to catalyst grafting aiming at separating the active metallocene from the silica surface has led to an increase in activity [11–13].

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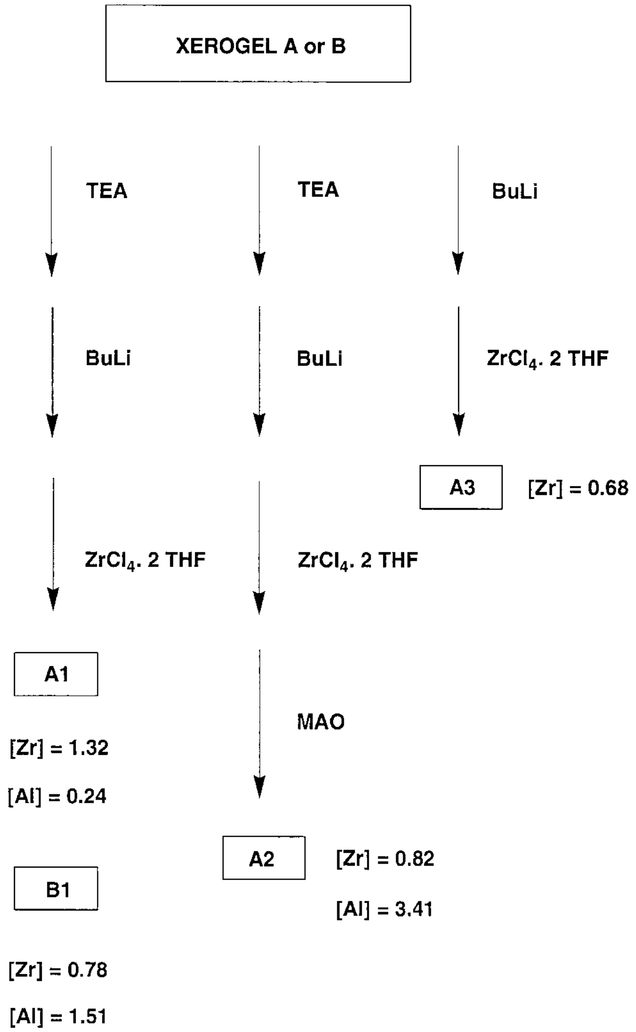

Scheme 1.

One approach to overcome these problems is the development of organic–inorganic hybrid xerogels already containing the metallocene ligands. The synthesis of such materials in which organic molecules or building blocks are combined with structural elements of ceramic materials aims at widening or improving xerogel properties without influencing the existing ones, such as heat insulation, transparency, and high surface area [14–16].

The most effective way to generate such hybrid xerogels is by the covalent binding of the organic groups. In the case of silicate systems, because of the hydrolytic stability of Si–C bonds, precursors can be used where the functional organic group is bonded through a stable Si–C link to the network-forming inorganic part of the molecule [17].

In situ-supported metallocene synthesis has already been reported in the literature, but generally they consist of constructing all or part of the ancillary ligand set on the commercial support prior to reaction with the metal compound [8,18–20]. In a previous work [21], we reported the synthesis and characterization of two silica xerogels prepared by the sol–gel method containing indenyl groups (Ind_2SiO_2) on their surface. Such xerogels were employed in the preparation of supported metallocenes [22], which were shown to afford a much higher metal content.

In the present paper we evaluated the effect of polymerization conditions (Al/Zr ratio, temperature, cocatalyst, comonomer concentration) on ethylene polymerization and on ethylene/1-hexene copolymerization activity using four supported catalysts developed by the sol–gel method. One of the employed xerogels was characterized by small-angle-X ray spectroscopy (SAXS) in order to evaluate its chemical structure and potentiality in breaking up during polymerization. The resulting polymers were characterized by differential scanning calorimetry, gel permeation chromatography and ^{13}C-NMR spectroscopy. X-ray photoelectronic spectroscopy (XPS) provided a residual metal content in the polymer films.

2. Experimental part

2.1. Materials

Indene (+85%, Kanto Chemical. Co., Japan) and tetraethyl orthosilicate (extra pure reagent, Nacalai Tesque Inc., Japan) were purified by vacuum distillation. Toluene (extra pure grade, from Nacalai Tesque Inc., Japan), tetrahydrofuran (THF, first grade from Kanto Chemical. Co., Japan), diethylether (first grade, from Wako Pure Chemical Industries Ltd, Japan), heptane (extra pure grade, from Nacalai Tesque Inc., Japan) and 1-hexene (first grade, from Wako Pure Chemical Industries Ltd, Japan) were purified according to the usual procedures. Zirconium tetrachloride ($ZrCl_4$, +98%, Merck-Schuchardt, Germany), diethoxydichlorosilane (ShinEtsu, Japan) and butyllithium (*n*-BuLi, reagent grade in hexane solution, from Kanto Chemical Co. Inc., Japan) were used without further purification. Ethylene (polymerization grade, Takachiho Trading Co. Ltd, Japan) was purified with columns of NaOH (extra pure grade, from Nacalai Tesque, Inc., Japan) and P_2O_5 (+98.9%, from Wako Pure Chemical Industries Ltd, Japan). Methylaluminoxane (MAO, in toluene solution), trimethylaluminum (TMA), triethylaluminum (TEA) and triisobutylaluminum (TIBA) were donated by Tosoh Akzo Co., Japan and were used without further purification.

2.2. Synthesis of indenyl-silica

Synthesis of diindenyldiethoxysilane is reported elsewhere [21]. Modified xerogels (Ind_2SiO_2) were prepared by hydrolysis and condensation reactions of $Si(OEt)_4$ (TEOS) and $(EtO)_2SiInd_2$ under two deliberate conditions. In route A, the component ratio TEOS:$(EtO)_2SiInd_2$ was 5:1, water corresponding to the half of the number of ethoxy groups. The reaction was carried out in toluene at 80°C for 6 h without the catalyst. In route B, the TEOS:$(EtO)_2SiInd_2$ ratio was 3:1, with an added amount of water corresponding to the total consumption of the ethoxy groups. The reaction was performed in ethanol at 30°C for 60 h, using 0.01 N NH_4OH solution as catalyst. Both xerogels A and B were employed to produce supported catalysts.

2.3. Synthesis of the catalysts

The supported catalysts were prepared according to three different routes (Scheme 1). In route 1, the xerogel A was reacted with 10 cm^{-3} of TEA (1 mmol of Al cm^{-3}) for 16 h. The resulting solid was then reacted with 6 cm^3 of *n*-BuLi hexane solution. (70°C for 8 h) and stirred continuously at room temperature (16 h). After removing the solvent, the solid was washed with hexane (3×30 cm^3) and vacuum dried. In a two-neck flask equipped with a dropping funnel and a magnetic stirring bar, 1.0 g of treated $IndSiO_2$ was dissolved in 40 cm^3 of THF, followed by the dropwise addition of 5 mmol of $ZrCl_4 \cdot 2THF$ in 50 cm^3 of THF at room temperature. The resulting brown solid was washed with THF (3×30 cm^3) and dried under vacuum. The slurry was then transferred to a fritted disk, washed with THF (25×2 cm^3) and the resulting solid dried under vacuum.

In route 2, the same procedure described above was performed but with an additional step. The resulting solid obtained in route 1 was further reacted with 12 cm^3 of MAO toluene solution (1 mmol Al cm^{-3}) at room temperature for 18 h. The catalyst was then washed with toluene (5×30 cm^3) and dried under vacuum.

The third route was performed by reacting xerogel A with 9 cm^3 of *n*-BuLi at room temperature, followed by refluxing for 8 h. To the resulting solid, 2 mmol $ZrCl_4 \cdot 2THF$ in THF was added at room temperature. The resulting solid was washed with 20×5 cm^3 of hexane and dried under vacuum.

Catalyst B1 was synthesized according to the procedure described in route 1, using xerogel B instead of A as the support.

Metal contents (expressed in mmol Zr or Al/g-cat.) of the resulting solids are reported in Scheme 1.

2.4. Polymerization procedure

The measured amounts of toluene, cocatalyst and catalyst slurry were introduced to a 100 cm^3 stainless steel autoclave equipped with a magnetic stirrer. After stirring at room temperature for 30 min., the system was degassed at liquid nitrogen temperature. After introducing 0.29 mol of ethylene monomer (7 dm^3 at STP), polymerization was initiated by rapidly warming up to the polymerization temperature. The polymerization was terminated by adding acidic methanol. The precipitated polymers were washed with methanol and dried under vacuum at 60°C for 6 h.

2.5. Analytical procedures

2.5.1. Characterization of the supports and the catalysts

SAXS experiments were performed in a MI8XHF instrument using CuKα as the source and PSPC as the detector. Analyses were performed at 40 kV and 30 mA.

XPS were taken with an Alvac PHI5600 Esca System with monochromated AlKα X ray radiation (1486.6 eV) at 300 W. Acquisition was carried out at room temperature in high-resolution mode (0.1 eV step, 23.5 eV pass energy) for the C1s, Al2p and Zr3d regions. The samples were mounted as thin polymer films, introduced into a transfer chamber and then evacuated to 10^{-6} Torr for 90 min using a turbomolecular pump. During data collection (takeoff angles of 75°), an ion-getter pump was used to maintain the pressure in the analysis chamber under 10^{-9} Torr.

The surface atomic ratios were calculated from the integrated areas of the spectra. The sensitivity factors employed were (C(1s) 2.019, Al(2p) 56.65 and Zr(3d) 36.49), empirically derived for the electron energy analyzer supplied by Perkin–Elmer.

2.5.2. Characterization of the polymers

The polymer melting points (T_m) were measured by differential scanning calorimetry (DSC), in a Seiko DSC 220C. The analyses were performed with a heating rate of 10°C min^{-1} in the temperature range of 25–200°C. The heating cycle was performed twice, but only the results of the second scan were recorded.

^{13}C NMR analysis of the copolymers was recorded at 140°C on a Varian Gemini 300 spectrometer operating at 75 MHz. The solution was made up in 1,2,4-trichlorobenzene/C_6D_6 (volume ratio = 9/1) up to 10 wt%.

Molecular weight and molar mass distribution (MMD) of the polymers were measured at 145°C by gel-permeation chromatography (GPC, Senshu Scientific, SSC7100) using *o*-dichlorobenzene as solvent.

3. Results and discussion

The four catalysts discussed here were prepared using two different xerogels (named A and B), treated at different conditions. ^{13}C MAS-NMR spectroscopy analysis of the xerogels in the low-field region showed signals at 142.1, 144.1 and 110.6 ppm, which were attributed to indenyl groups. Besides, the presence of ethoxy moieties was also detected by the presence of signals at 60.7 and 19.1 ppm [21]. The presence of such groups on the gel surface is very common. For instance, aerogels made from $Si(OMe)_4$ exhibit 30% of their silicon atom still carrying a methoxy substituent [23]. Nevertheless, the presence of such ethoxy groups demanded the previous chemical treatment of the support prior to metallation with $ZrCl_4 \cdot 2THF$. The two aerogels were then treated with TMA (route 1) and BuLi (route 3) while, in the case of A2, the catalyst obtained by route 1, was further treated with MAO.

^{29}Si MAS NMR analysis of the xerogels showed signals at −48.6, −70.0 and −101.8 ppm [21]. The first two signals were attributed to monodentate and tridentate species, while the third was attributed to Si atoms present in the Si–O–Si network. In other words, bidentate species, which could be

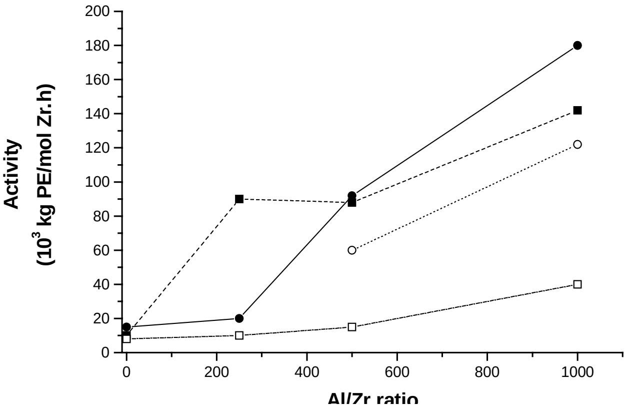

Fig. 1. Influence of the Al:Zr molar ratio on ethylene polymerization activity using supported catalysts: (■) A1, (●) A2, (□) A3 and (○) B1. Polymerization reactions were performed in toluene at 70°C with [Zr]-0.01 mmol ml^{-1} (MAO cocatalyst).

comparable to Ind_2ZrCl_2 (a model soluble metallocene system), are absent, probably because of the steric effect played by the huge indenyl groups during condensation reactions. The four catalysts were characterized by complementary spectroscopy techniques: ICP, UV–Vis, DRIFTS, XPS, ^{27}Al and ^{13}C CP-MAS, MALDI-TOF-MS (matrix-assisted laser desorption ionization time-of-flight mass spectroscopy), SEM, EMPA (electron probe microanalysis) [22]. Monodentate and bidentate zirconocene fragments were confirmed by MALDI-TOF-MS analyses of the catalysts [22].

The effect of some ethylene polymerization conditions (Al/Zr ratio, temperature, cocatalyst, comonomer concentration etc.) on the catalyst activity, using such catalysts will be discussed in the following sections.

3.1. *Effect of the Al/Zr ratio*

Fig. 1 shows the effect of the Al/Zr in ethylene polymerization, employing MAO as cocatalyst. All the four catalysts were shown to be dependent on the Al/Zr ratio present in the milieu, highest activity being at Al/Zr = 1000. The highest activity was exhibited by A2 being directly dependent on the MAO content. The highest activity of such a catalyst system was attributed to the presence of lower binding energy species determined by XPS measurements [22]. Moreover, according to EMPA, such systems present a better Zr distribution around the xerogel particle, being covered by an Al layer [22]. According to Scheme 1, A1 catalyst system presents the highest Zr content (1.32 mmol/g-cat.). Nevertheless a reduction of 38% of the initial concentration was observed after MAO treatment (compare the metal content between A2 and A1). Leaching of metallocenes by MAO has been reported in the literature [24]. It is believed that MAO is capable of cleaving Si–O–Zr bonds. It is worth noting that we cannot neglect the possibility that under polymerization conditions (Al/Zr = 1000, and 70°C), some supported metallocene is leached to the solution thus acting as a soluble catalyst. Nevertheless, M_w of the resulting polymers is much higher than those usually obtained with homogeneous catalysts, suggesting that leaching if occurred is not the predominant species. Moreover, the eluent solution resulting from the washing of the A1 system did not present catalyst activity in ethylene polymerization. It is very likely that MAO treatment removes unreactive zirconocene species consequently leading to most active systems.

It is worth mentioning that the activity exhibited by such catalyst systems is much higher than that reported by supported catalysts commonly obtained by conventional procedures of grafting metallocenes on commercial silica. For instance, 1×10^3 kg PE mol Zr h^{-1} was reported for $(n\mathrm{BuCp})_2ZrCl_2/SiO_2$ when cocatalyzed by MAO at Al/Zr = 2000 [25]. A similar catalyst activity was reported in the case of $CpIndZrCl_2$/silica containing pentamethylene spacer, using MAO in Al/Zr = 5000 [26].

In the absence of cocatalyst (Al/Zr = 0), all the systems exhibited extremely low activities. Nevertheless, A2 was shown to be the most active among the four catalysts under such conditions. The catalyst activity in the absence of MAO or other external cocatalyst has already been reported in the literature in the case of MAO-modified supports, and associated to the generation of cationic active species on the surface [27]. In the present case, A2, besides the support treatment with TEA, was also treated with MAO after metallation. UV–Vis analysis of the catalyst showed a large band centered at 320 nm and shoulders at 360 and 420 nm [22], with the last two being attributed to the precursor methyl derivative [28] and dimethyl derivative [29], respectively.

A2 was also tested in propylene polymerization at 40°C and at Al/Zr = 1000. The catalytic activity was rather low generating mostly atatic polypropylene. These results are completely different from those obtained with homogeneous $Et(Ind)_2ZrCl_2$ tested at the same polymerization conditions, which exhibited 4.0×10^4 kg PP mol Zr h^{-1} of the catalytic activity. The extremely lowest activity observed in the case of the supported system can be partially attributed to a different nature of the generated surface species from that present in solution in the case of the homogeneous catalyst.

Table 1 presents polymer properties of the resulting polyethylenes. According to GPC measurements, M_w of the resulting polymer is very high ($\approx 10^{-6}$ g mol^{-1}). A higher molecular weight for polymers obtained with supported metallocenes has already been reported in the literature [25], and this behavior has been attributed to the fact that immobilized metallocenes on the surface hinders the bimolecular reaction between the two catalytic centers, which might lead to β-hydrogen transfer [27]. Therefore, this enables a longer growth of the polymer chain, resulting in a polymer with higher molecular weights.

Molecular weight distribution (ca. 2.5–2.8) is roughly of the same order as usually reported for supported metallocenes. Catalyst system A3 showed a much higher

Table 1
Polymer properties of polyethylene produced with different supported metallocene catalysts (polymerization conditions are: [Zr] = 0.01 mmol l^{-1} (toluene); temperature = 70°C; reaction time = 0 min.; ns = not soluble)

Al/Zr	Catalyst system								
	A1			A2			A3		
	M_w (10^{-6})	M_w/M_n	T_m (°C)	M_w (10^{-6})	M_w/M_n	T_m (°C)	M_w (10^{-6})	M_w/M_n	T_m (°C)
1000	1.1	2.8	143.7	1.0	2.4	143.2	1.0	3.8	141.8
500	ns	–	143.6	0.9	2.5	141.7	1.6	8.2	141.6
250	3.0	3.8	141.7	0.6	2.8	141.8	1.5	12.4	142.5

polydispersity index (PDI), suggesting a broader heterogeneity in the nature of the active sites. The full width at half maximum intensity (FWHM) of a peak at XPS analysis is an indicative of the species distribution. XPS spectra of these catalysts are reported elsewhere [22]. Considering the $Zr3d^{5/2}$ signal situated ca. 181.0 eV, the FWHM values increase in the following order: A2 (2.5 eV), A1 (2.6 eV) and A3 (3.1 eV), being in accordance with the observed PDI.

It is worth noting that the fact of working under batch conditions may impart some broadening in the PDI due to ethylene transfer reaction rate, which shall be different at the early beginning of the reaction in comparison to the later polymerization times. Nevertheless, as the reaction time is relatively short, we can neglect the effect of the monomer (or comonomer) concentration on the molecular weight and on the PDI.

3.2. *Effect of the temperature*

The influence of the temperature on the catalyst activity was evaluated at 40, 70, 100 and 120°C, for a constant Al/Zr = 500. Fig. 2 shows the results for A1 and A2 catalysts. In the case of A1, the highest activity was attained at 70°C, thereby decreasing for higher temperatures. On the other hand, catalyst activity of A2 increases from 40 to 70°C, maintaining a roughly constant activity for temperatures as high as 120°C.

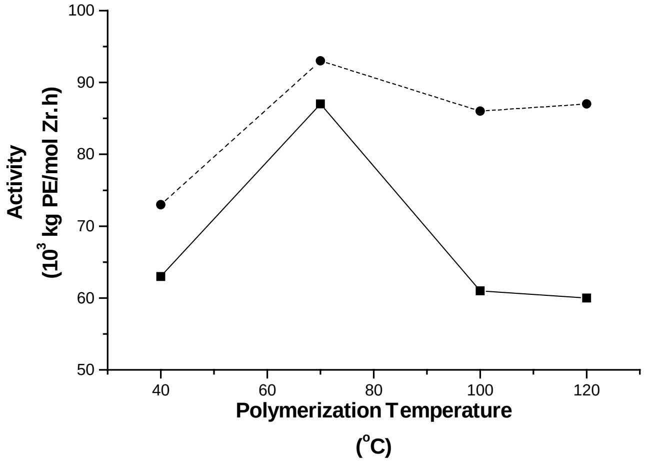

Fig. 2. Influence of the polymerization temperature using: (■) A1; (●) A2. Polymerization reactions were performed in toluene at Al/Zr = 500 with [Zr] = 0.01 mmol ml^{-1} (MAO cocatalyst).

The influence of the temperature on metallocene polymerization has already been reported in the literature. A similar trend observed in the case of A1 has already been reported for homogeneous *ansa*-metallocene catalysts [30]. A widely accepted mechanism of propagation in Ziegler–Natta catalysis involves the initial formation of a π-complex of an olefin with the metal catalyst, followed by a chain migratory insertion [31]. At high temperatures, however, the complex readily dissociates. Although the olefin polymerization rate is expected to increase with the increasing polymerization temperature in the low-temperature domain, the trend should be reversed at the high-temperature domain, and may be complicated by the deactivation of the catalytic species. Deactivation usually takes place at high temperatures, although little is known about the possible chemical transformations of metallocenium species. Thus for A1 the reduced catalytic activity in the polymerization performed at temperatures higher than 70°C can be attributed to both the low-propagation rate and catalyst deactivation. Nevertheless, it appears that deactivation is reduced in the case of catalyst A2 which exhibited almost a constant activity even in a temperature as high as 120°C.

Therefore, the different behaviors of both catalysts at increasing temperatures can be in part caused by a different thermal stability of the catalysts, and by the stability of the surface species generated on the support after activation with the cocatalyst.

3.3. *Effect of the cocatalyst*

The usually high amounts of MAO, which is necessary to maintain high activity, alliated to its high costs have led to the search of new alternative cocatalysts. Among them, the common alkylaluminuns [32], borates [33–36] and more recently, perchlorates [37] have been proposed as alternative cocatalysts for metallocene systems.

Table 2 presents the catalyst activity in ethylene polymerization performed at 70°C in Al/Zr = 1000. For comparative reasons, data from MAO as cocatalyst were also included. All the systems were shown to be active in the presence of common alkylaluminum compounds. Nevertheless, a

Table 2
Catalyst activity in ethylene polymerization. [Al]/[Zr] = 1000. Temperature: 70°C. [Zr] = 0.01 mmol ml^{-1} (polymerization conditions as follow: [Zr] = 0.01 mmol l^{-1} (toluene); [Al]/[Zr] = 1000; temperature = 70°C; reaction time = 30 min)

	Catalyst system[a]			
	A1	A2	A3	B1
MAO	143	180	40	130
TMA	40	12	4.7	–
TEA	93	17	2.9	–
TIBA	36	40	1.0	32

[a] Catalyst activity expressed in 10^3 kg PE/mol Zr h^{-1}.

reduction in the catalyst activity was observed on comparing these data with those performed with MAO. Trialkylaluminum behaves in the same way as MAO, but the resulting anion coordinates the metallocene cation strongly [38]. On the contrary, MAO anion, quite cumbersome and less coordinate, maintains the cation available enough for the olefin insertion [39]. MAO has a suitable alkylating capability and Lewis acidity (it is stronger Lewis acid than TMA because of the adjacent eletronegative oxygen atoms in its structure) and it is bulky enough to avoid strong coordination with the cation.

Among the three tested systems, no clear tendency related to the effect of the nature of the alkylaluminum compound could be established. In the case of A1, TEA was shown to be more effective, while in A2, TIBA showed the best performance. TMA afforded a higher catalyst activity only in the case of A3. This catalyst was shown to present residual silanol groups even after BuLi treatment [22]. Probably the better performance of such cocatalyst in the case of A3 could be explained by its higher reactivity with surface silanol groups comparing with the two other alkyl compounds.

3.4. Catalyst aging

The effect of catalyst aging was evaluated for catalyst A2, in ethylene homopolymerization using Al/Zr = 500 with the polymerization temperature at 70°C, for six months. The solid catalyst was kept under Ar during this period.

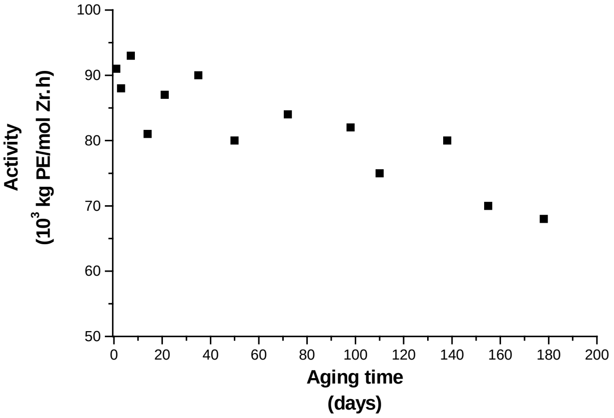

Fig. 3. Effect of A2 aging on catalyst activity. Polymerization reaction were performed in toluene at 70°C with [Zr] = 0.01 mmol ml^{-1} (Al/Zr = 500).

Fig. 3 shows the effect of catalyst aging on the catalyst activity. According to Fig. 3, A2 showed to be stable for a period up to six months, showing no significant loss of activity. Higher stability is expected for supported catalysts, in which the bimolecular deactivation is avoided by the fact that the active species should be kept apart from each other on the support surface.

3.5. 1-Hexene/ethylene copolymerization

The prepared supported catalyst systems were evaluated by 1-hexene/ethylene copolymerization. The comonomer concentration in the polymerization milieu was varied from 0.26 to 2.60 mol cm^{-3}. Copolymerization reactions were performed at 70°C in Al/Zr = 1000.

Fig. 4 reports the catalyst activity for the three supported systems. For comparative reasons data of ethylene homopolymerization ([hexene-1] = 0.0 mol cm^{-3}) were also included.

The catalytic activity was shown to be sensitive to the comonomer concentration. For the three systems, the copolymerization catalytic activity is higher than that for homopolymerization. This behavior is known as the *comonomer effect*, which is typical for Ziegler–Natta catalysts, and has been also previously reported for MAO-activated zirconocenes [40–43]. This could be attributed to the higher solubility of the copolymer in the reaction milieu, which might allow higher diffusion rates of the monomers onto the active sites, therefore, enhancing the copolymerization activity. The decrease in catalyst activity for monomer concentrations higher than 1.30 mol cm^{-3} might be associated with an increase of comonomer in the polymeric growing chain, which in turn leads to a

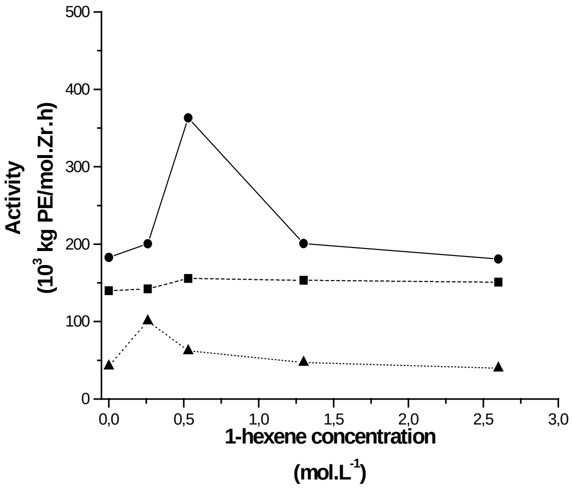

Fig. 4. Influence of the comonomer concentration on copolymerization activity using supported catalysts: (■) A1, (●) A2, (▲) A3. Copolymerization reactions were performed in toluene at 70°C with [Zr] = 0.01 mmol ml^{-1} (MAO cocatalyst).

reduction in activity because of a decrease in the propagation rate with the comonomer incorporation.

The properties of the resulting copolymers are shown in Table 3. The increase of the 1-hexene incorporation in the polymer chain leads to a reduction in the crystallinity (X_c). Even a small amount of comonomer incorporation causes a noticeable reduction in crystallinity as we can observe by comparing the ethylene homopolymer to the resulting copolymers.

A similar trend can be observed in the melting point (T_m) of the copolymers. As the 1-hexene incorporation rises, the loss of crystallinity causes a reduction in the melting temperature of the material.

‘The low comonomer incorporation of the supported systems can be attributed to a steric effect played by the silica surface, which reduces the accessibility of the comonomer onto the active sites. Among the three tested catalyst systems, A2 showed the highest activity. For 1-hexene concentration higher than 1.3 mol cm^{-3}, the incorporated comonomer content is slightly higher than that reported in the case of silica-supported metallocenes [44].

The decrease in the molecular weight with comonomer incorporation suggests that 1-hexene incorporation favors chain termination reactions with the comonomer (β-H elimination), consequently leading to lower molecular weight copolymers.

3.6. Xerogel A fractal dimension

In order to evaluate the potentiality of these catalysts, a better insight in the support properties is necessary. Alkoxide silica gels are produced from hydrolysis and polymerization of alkoxides. In the first step, water hydrolyzes successive alkoxide groups to create silanols and the corresponding alcohol:

$$\equiv \text{Si–OR} + H_2O \rightarrow \equiv \text{Si–OH} + \text{ROH} \tag{1}$$

where R is an alkyl group (commonly –Me or –Et).

Subsequent to hydrolysis is polymerization by silanol condensation, where siloxane (Si–O–Si) bonds are formed.

$$\equiv \text{Si–OH} + \text{HO–Si} \equiv \rightarrow \equiv \text{Si–O–Si} \equiv + H_2O \tag{2}$$

$$\equiv \text{Si–OH} + \text{RO–Si} \equiv \rightarrow \equiv \text{Si–O–Si} \equiv + \text{ROH} \tag{3}$$

The ratio between both reactions influences the texture properties of the resulting xerogel. Porous materials has been also characterized by SAXS in the literature [45,46]. In the present work, SAXS data were fitted using the model proposed by Emmerling et al. [47]

$$I(q) = I_0[B + V_0 S(q) P(q)] \tag{4}$$

where I_0 is the normalization constant, B a constant background from the sample and V_0 the mean volume of the primary particles. $P(q)$ is the form factor and $S(q)$ is the structure factor describing the packing of the primary particles.

Assuming nearly spherical primary particles with radius R, we can assume:

$$V_0 = \frac{4\pi R^3}{3} \tag{5}$$

$$P(q) = \frac{1}{\left[\dfrac{1 + 2^{1/2}(qR)^2}{3}\right]^2} / \tag{6}$$

$$S(q) = 1 + \left(\frac{C(D)}{qR}\right)^D \tag{7}$$

Table 3
Properties of the polymers obtained by the three supported catalysts (polymerization conditions are: [Zr] = 0.01 mmol l^{-1} (toluene); temperature = 70°C; Al/Zr = 1000; reaction time = 30 min; nd = not determined)

Initial [1-hexene] mol cm^{-3}	T_m (°C)	X (%)	M_w (10^{-5})	M_w/M_n	Incorporated 1-hexene (%)
Catalyst A1					
0.00	143.7	72	11.0	2.8	–
0.26	137.3	54	1.9	2.1	nd
0.53	134.2	47	1.8	3.0	nd
1.30	131.7	44	2.1	3.3	5.0
2.60	126.1	41	1.5	3.4	6.8
Catalyst A2					
0.00	141.7	85	10.0	2.4	–
0.26	133.6	50	1.4	3.5	nd
0.53	129.3	47	1.8	3.8	nd
1.30	128.6	36	2.8	3.7	5.0
2.60	124.3	34	1.6	5.2	7.4
Catalyst A3					
0.00	141.8	96	10.0	3.8	–
0.26	142.1	97	1.6	3.4	nd
0.53	141.8	85	2.2	2.6	nd
0.26	140.3	83	1.7	3.3	5.1
3.60	139.2	65	1.5	3.1	6.3

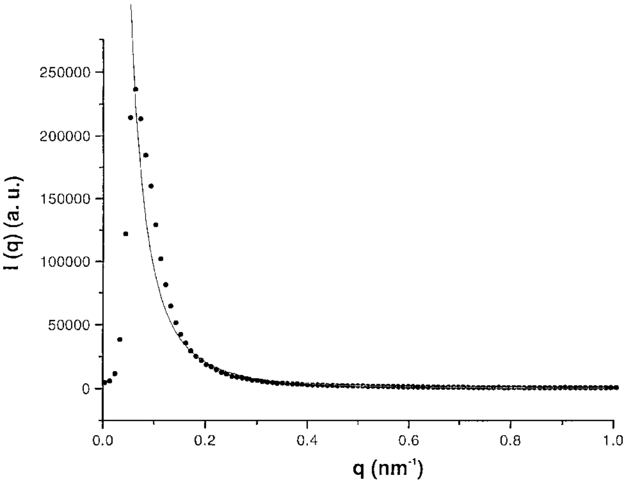

Fig. 5. SAXS intensity, *I*(*q*) as a function of scattering vector *q* for Xerogel A. The full line shows the fit used to determine the particle radius *R* and fractal dimension *D*.

where *D* is the fractal dimension of the aggregate and *C*(*D*) is a constant depending on *D* [47].

$$C(D) = \frac{D\Gamma(D-1)\sin[\pi(D-1)]}{2} \tag{8}$$

Fig. 5 shows the scattering curve of xerogel A and the fitting obtained to these experimental results. The fit yields three parameters: the background *B*, the particle radius *R* and fractal dimension *D*. Good fitting was obtained in 4 orders of magnitude in the intensity and 2 orders of magnitude in *q* having $B = 0.02$ and $R = 6.5$. The particle radius is in the same range as measured by SEM.

The fractal dimension *D* is a measure of the degree of branching of the network formed by the primary particles. According to the fitting, the fractal dimension was 1.33. Values lower than 2.30 indicates that the network is formed by the cluster–cluster aggregation rather than by monomer–cluster aggregation [48]. In other words, during the xerogel synthesis, hydrolysis reactions were faster than condensation. This tends to produce weakly branched polymeric networks [49].

Low *D* values has been attributed to the participation of both TEOS and alkoxysilanes in the built-up of the gel. Such conditions might favor a structure more prone to break up during the polymerization reactions increasing the access of new catalyst site.

3.7. Polymer residual metal content

Polymers produced by metallocenes have been reported to be chemically stable due to low residual metal content in comparison to those produced by Ziegle–Natta or Philips catalysts [50]. In turn this low-residual metal content is a consequence of the extremely high activity shown by metallocenes cocatalyzed by MAO. It is worth mentioning that besides catalyst stability, low residual metal contents are necessary to avoid coloring and toxicity of the employed materials.

We determined the residual metal content of PE produced with A2 catalyst, at $\mathrm{Al/Zr} = 1000$. According to XPS measurements performed in the high-resolution mode, the $\mathrm{Zr/C} = 0.00$ and $\mathrm{Al/C} = 4.0 \times 10^{-3}$. Based on ICP measurements, we can roughly estimate that the Zr content should be lower than 0.01 ppm. Similar magnitude values for Al/C were reported in the measurement of residual metal content in polymers produced by metallocene catalyst system and determined by Rutherford Backscattering Spectrometry (RBS) [51].

4. Conclusions

Supported metallocene catalysts prepared using xerogels containing indenyl groups were shown to be very high-activity systems for ethylene polymerization and ethylene/1-hexene copolymerization, even in the presence of common alkylaluminum (TMA, TEA, TIBA). Depending on the preparative conditions, such catalyst systems present thermal stability up to 120°C. Owing to their high activity, residual zirconium content on the polymers produced is very low. 1-Hexene incorporation was relatively high in comparison to other metallocene-supported catalysts. Further experiments have been carrying on concerning the development of similar catalysts prepared by the sol–gel method containing other ligands.

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