

The Influence of Bridge Type on the Activity of Supported Metallocene Catalysts in Ethylene Polymerization^{*}

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Abstract Ethylene polymerization was carried out by immobilization of *rac*-ethylenebis(1-indenyl)zirconium dichloride ($\text{Et}(\text{Ind})_2\text{ZrCl}_2$) and *rac*-dimethylsilylbis(1-indenyl)zirconium dichloride ($\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$) preactivated with methylaluminoxane (MAO) on calcinated silica at different temperatures. Polymerizations of ethylene were conducted at different temperatures to find the optimized polymerization temperature for maximum activity of the catalyst. The Me_2Si bridge catalyst showed higher activity at the lower polymerization temperature compared to the Et bridge catalyst. The highest catalytic activities were obtained at temperatures about 50 °C and 70 °C for $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ and $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalysts systems, respectively. Inductively coupled plasma-atomic emission spectroscopy results and polymerization activity results confirmed that the best temperature for calcinating silica was about 450 °C for both catalysts systems. The melting points of the produced polyethylene were about 130 °C, which could be attributed to the linear structure of HDPE.

Keywords: Slurry polymerization; Olefin polymerization; *ansa*-Metallocene; Silica support.

INTRODUCTION

The production of polyolefins such as polyethylene (PE) and polypropylene (PP) and their copolymers grows rapidly because of their outstanding product properties and environmental compatibility^[1]. Metallocene catalysts have opened a new field in the polymerization of olefins^[2, 3]. These catalysts show a single site active center behavior, making it possible to design the structure of the polymer precisely. In comparison with conventional Ziegler-Natta catalysts, which have multi active sites and produced polymers with broad MWD, metallocene catalysts have a much higher activity and lower polydispersity index^[4–6]. Homogeneous metallocene catalysts can be stereospecific in polymerization process and they can produce polymer with narrow MWD^[4]. Unfortunately, homogeneous metallocenes require large amounts of expensive MAO to yield maximum catalyst activity. This, to some extent, may impair their commercial application. Therefore, much effort has been made not only to lower the amount of MAO in polymerization, but also to find a new cocatalyst to replace it. Furthermore, metallocene and late transition metal catalysts need to be supported^[7–11] to allow their use in gas- and slurry-phase process and prevents reactor fouling and enabling formation of uniform particles with narrow size distribution and high bulk density. In addition, supported systems need smaller amount of MAO than

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homogeneous systems^[8].

The immobilization of metallocene/MAO systems on silica supports is generally carried out by contacting the metallocene with a MAO impregnated support, or by first contacting metallocene and MAO to generate the active species before immobilization on the support^[8]. A review of the literature shows that studies investigating the influence of silica calcination temperature on heterogenizing metallocenes, particularly $(\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2)$ for ethylene polymerization, are fairly limited. In the present study, silica was calcinated at different temperatures to obtain support with different contents of hydroxyl groups and the effects of calcination temperatures and the structure of metallocene on the activity of polymerization have been investigated.

EXPERIMENTAL

Materials

All reactions were carried out under nitrogen atmosphere. A 10 wt% solution of methylaluminoxane (MAO) in toluene (used without further purification), and *rac*-ethylene-bridged bis(indenyl) zirconium dichloride, $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ was purchased from Aldrich. *Rac*-dimethylsilyl-bridged bis(indenyl) zirconium dichloride, $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ was purchased from Chemos. Silica ES70W was kindly donated from Ineos silica and alumina technology, having a surface area of 295 m²/g, an average pore volume of 1.6 mL/g, a particle size 41 μm and an average pore size of 21 nm. *n*-Heptane (less than 1×10^{-6} mol/L H₂O) was purified by refluxing over sodium and by distilling, as described in the literature^[12, 13]. Ethylene and nitrogen (99.9995% pure) gas were prepared from Petrochemical Researching and Technology Company.

Silica Calcinations and Characterization

Calcination of the silica supports was carried out at 200 °C, 450 °C and 600 °C under a N₂ flow (20 mL/min). Each support was heated at 10 K/min until the desired temperature was reached and then held isothermally for 4 h. Afterward, the sample was allowed to cool to ambient temperature. Surface area was determined using the Brunauer Emmet Teller (BET) method, while the pore volumes and pore diameter were determined by the Barrett Joyner Halenda (BJH) method for mesoporous materials.

Catalyst Preparation and Characterization

All experiments were performed under inert atmosphere in the glove-box under the purge of the dry nitrogen gas. 0.04 g metallocene catalyst, followed by 8 mL of 10 wt% MAO in toluene solution, was added into a degassed vial equipped with a magnetic stirring bar inside the glove box. The mixture was stirred at room temperature for 30 min; afterward, 1 g of silica dehydrated was added to the mixture while metallocene/MAO was under constant stirring. The mixture was stirred for 6 h; then the solvent evaporated and the catalyst was dried by nitrogen purge which was followed by vacuum evacuation. A yellow free-flowing solid was obtained at the end of the preparation process. Following the complete drying of the catalyst, 50 mL of the dry heptane was added to the powder of supported metallocene catalyst and stirred until a steady suspension of the catalyst in heptane was obtained. Zirconium and aluminum contents of the resulting supported metallocene/MAO catalyst were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) after HF acid digestion of the solid. The morphology of the samples was investigated by using a Philips scanning microscope XL-30.

Ethylene Polymerization

Ethylene polymerization was carried out in a 1 L Buchi reactor equipped with an impeller and temperature control. Before each polymerization run, the temperature was set at 95 °C and the reactor was purged with nitrogen for 2 h to remove air, humidity and other impurities completely. Temperature was decreased to polymerization temperature and 500 mL heptane was added to the reactor after completion of purging procedure. 2.5 mL of triethylaluminum (TEA) (1 mol/L in heptane solution) was charged into the reactor for scavenging. For each experiment, 4.5 mL of the suspended catalyst as prepared in the previous section was added to reactor

under nitrogen atmosphere. Polymerization reactions were carried out at 40 °C, 50 °C, 60 °C and 70 °C for 30 min under 0.75 MPa of ethylene pressure. Acidified (HCl) ethanol was used to quench the process, and reaction products were separated by filtration, washed with distilled water, and dried.

Polymer Characterization

The obtained polymers were characterized with scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and viscometry. The morphology of polymer particles was studied using an SEM (Philips model XL-30). The DSC Mettler Toledo performing at heating rate of 10 K/min was used for the determination of the melting point within temperature range of 30 °C to 180 °C. According to ASTM D3417/97 and ASTM D3418/97, two scans were performed, but only the results of the second scan were reported. Viscosity average molecular weights were determined using solution viscosity method. The intrinsic viscosity $[\eta]$ of polymers was measured by using a Ubbelohde viscometer at 135 °C using decalin as the solvent. The viscosity average molecular weight (M_v) was calculated from a Mark-Houwink equation ($[\eta] = K \times M_v^\alpha$) using $K = 6.67 \times 10^{-3}$ mL/g and $\alpha = 0.67$ for polyethylene.

RESULTS AND DISCUSSION

Different methods are reported in the literature for efficient heterogenization catalyst precursors^[11, 14–16]. Immobilization is often accompanied by a significant decrease in catalyst activity, sometimes by as much as one order of magnitude relative to the homogeneous counterpart^[15]. For the specific case of immobilization of metallocene catalysts on silica, three methods are commonly used: (a) adsorbing metallocene onto a MAO-pretreated silica support; (b) reacting silica with a metallocene/MAO mixture and (c) supporting the metallocene and then reacting the product with MAO^[8].

Table 1 depicts the results of ICP measurements for the supported catalysts that calcinated at the temperature 450 °C. Zr and Al contents of the Et(Ind)₂ZrCl₂ catalyst were 0.41 wt% and 18.0 wt%, respectively. They were slightly higher than the respective amounts for Me₂Si(Ind)₂ZrCl₂ catalyst (Zr = 0.3 wt% and Al = 14.0 wt%). The [Al]/[Zr] ratio was essentially the same (*ca.* 45) for the two types of catalyst. Figure 1 shows the SEM image of the polymer particles obtained by Et(Ind)₂ZrCl₂ catalyst, the particles have average diameter around 200 µm. Somewhat reaction fouling could be observed in Fig. 1 that could be commonly happened, however by using MgCl₂ as carrier, different behaviors were observed as reported by Hou *et al.*^[16]

Table 1. ICP results for the two supported catalysts

Catalyst	Al wt%	Zr wt%	Al/Zr ratio
Et(Ind) ₂ ZrCl ₂	18	0.41	43.90
Me ₂ Si(Ind) ₂ ZrCl ₂	14.0	0.30	46.66

Calcination temperature = 450 °C, MAO = 12.2 mmol, silica = 1 g, [Zr] = 8×10^{-6} mmol

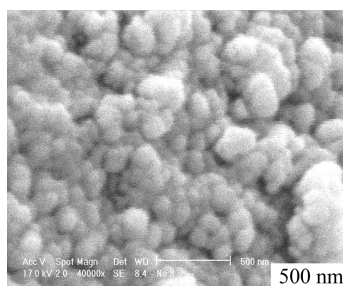


Fig. 1 SEM image of the polymer particles

Calcination temperature = 450 °C, MAO = 12.2 mmol, silica = 1 g, [Zr] = 8×10^{-6} mmol

Effect of Calcination Temperature

Figure 2 shows the Et(Ind)₂ZrCl₂/MAO and MeSi(Ind)₂ZrCl₂/MAO catalysts activities as a function of the silica

calcination temperatures. Activities are in the following order: $450\text{ }^{\circ}\text{C} > 200\text{ }^{\circ}\text{C} > 600\text{ }^{\circ}\text{C}$. This behavior can be attributed to the $[\text{Al}]/[\text{Zr}]$ ratio of the supported catalysts as measured by ICP (Table 2)^[17, 18]. It was found that the Zr content increased moderately as the calcinations temperature increased in the range of $200\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$, the Zr content was increased moderately at higher calcination temperatures; however on the other hand, calcination temperature has negligible influence on the Al loading of the impregnated support in the temperature range of $200\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$, (Table 2). As the calcination temperature is raised, an increment in the fraction of mono dentate species formed in immobilization, and consequently variation in catalytic activity was expected^[5]. Excess Zr loading at higher calcination temperatures around $600\text{ }^{\circ}\text{C}$ results in bimolecular metallocene deactivation as described in the literature^[19, 20]. It can lead to decrease of catalytic activities for both supported catalysts. The higher activity of $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ compared to $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ at all of calcination temperatures might be due to its higher Zr content as shown in Table 2.

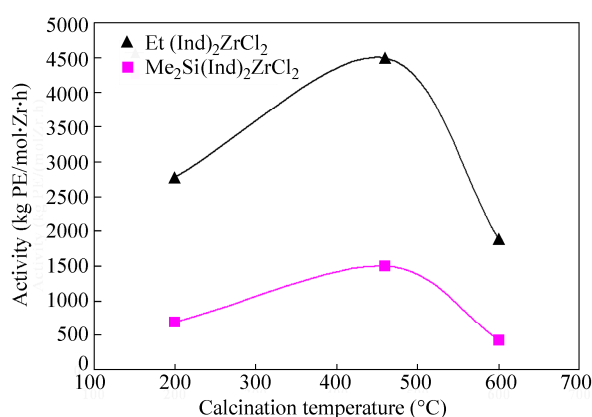


Fig. 2 Catalyst activities as a function of the calcination temperatures
[TEA] = 2.5 mmol, polymerization temperature = $50\text{ }^{\circ}\text{C}$, pressure = 0.75 MPa,
polymerization time = 30 min, $[\text{Zr}] = 8 \times 10^{-6}\text{ mmol}$

Table 2. ICP measurement at different calcination temperatures

Calcination temperature ($^{\circ}\text{C}$)	Et(Ind) ₂ ZrCl ₂ /MAO			Me ₂ Si(Ind) ₂ ZrCl ₂ /MAO		
	Al/Zr ratio	Zr wt%	Al wt%	Al/Zr ratio	Zr wt%	Al wt%
200	38.94	0.38	14.8	39.44	0.28	11.1
450	43.9	0.41	18	46.66	0.30	14.0
600	24.73	0.57	14.1	25.12	0.43	10.9

MAO = 12.2 mmol, silica = 1 g, $[\text{Zr}] = 8 \times 10^{-6}\text{ mmol}$

Effect of Polymerization Temperature

Figure 3 shows the effect of polymerization temperatures on the catalytic activities for $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ and $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ systems. Two metallocene catalysts show different trends with increasing polymerization temperature. Activity of $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst increased continuously with increasing polymerization temperature from $40\text{ }^{\circ}\text{C}$ to $70\text{ }^{\circ}\text{C}$ ^[21], while $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst showed a maximum at temperatures around $50\text{ }^{\circ}\text{C}$. The Me_2Si bridged catalyst showed higher activities at lower polymerization temperatures. The higher activity of Me_2Si bridged catalyst can be explained by comparing the steric conditions^[21, 22]. On the other hand at polymerization temperature above $60\text{ }^{\circ}\text{C}$ the Et bridged catalyst showed a higher activities compared to the Me_2Si bridged one. This trend can be attributed to the better thermal stability of the Et Bridge at higher temperatures^[22].

Polymer Characterization

Figure 4 shows M_v (viscosity average molecular weight) of polymers as a function of polymerization temperatures for $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ and $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ catalysts. Decrease of molecular weight at high polymerization temperatures is due to the enhanced chain-transfer reactions, which in turn, can be related to

higher activation energies for chain transfer reactions rather than the activation energy for propagation reaction.

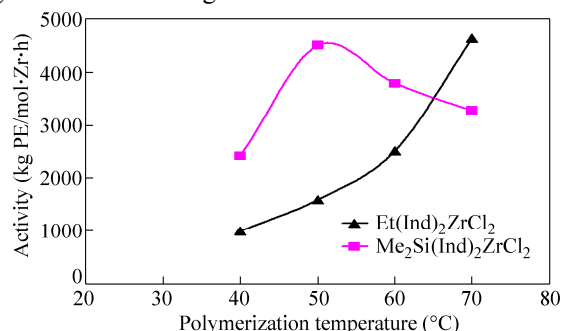


Fig. 3 The Effect of polymerization temperature on the activity of catalysts

Calcination temperature = 450 °C, [TEA] = 2.5 mmol, pressure = 0.75 MPa, time 30 min, [Zr] = 8×10^{-6} mmol

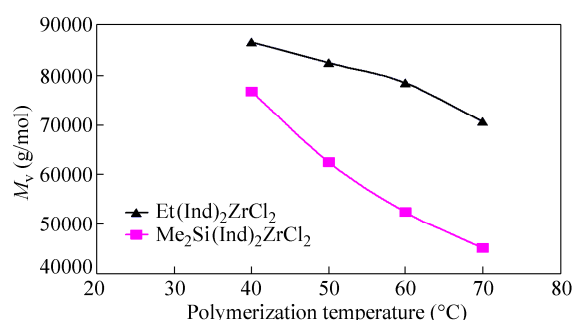


Fig. 4 The effect of polymerization temperature on M_n of the obtained polymers

Calcination temperature = 450 °C, [TEA] = 2.5 mmol, pressure = 0.75 MPa, time 30 min, [Zr] = 8×10^{-6} mmol

Polymers obtained by heterogeneous catalysts possess a higher molecular weight than that of the homogeneous one. This behavior, has been attributed to the blocking one side of polymerization active sites by the support which hinders the deactivation step. In other words, β -elimination transfer between two metallocene centers is hindered, resulting in additional growth of the polymer chain and hence, a higher molar mass^[14]. Comparing M_n of obtained polymers by the two catalysts in Fig. 4 reveals that the reduction rate is higher for Me₂Si(Ind)₂ZrCl₂ catalyst rather than Et(Ind)₂ZrCl₂ catalyst, which can be attributed to the lower thermal stability of Me₂Si bridge^[22].

Table 3 reveals the thermal properties of produced polymers. According to Table 3, both samples have approximately the same T_m (ca. 132 °C), but the polyethylene obtained with Et(Ind)₂ZrCl₂ catalyst was more crystalline than the one obtained by Me₂Si(Ind)₂ZrCl₂ catalyst. This trend can be easily explained by comparing M_n of the two polymers. Et bridged catalyst produces polyethylene with higher M_n and higher crystallinity compared to Me₂Si bridged catalyst. This is why polymers with a high average molecular weight show better mechanical properties than those with a low average molecular weight. This is an attractive feature of supported metallocene catalysts in general, and Et(Ind)₂ZrCl₂/MAO supported catalyst in particular^[21].

Table 3. DSC results of polyethylene obtained at polymerization temperature 70 °C

Catalyst	T_m (°C)		T_c (°C)		ΔH (J/g)	Crystallinity (%)
	Peak	Onset	Peak	Onset		
Et(Ind) ₂ ZrCl ₂	132.19	126.80	118.59	120.87	230.76	78.6
Me ₂ Si(Ind) ₂ ZrCl ₂	132.07	125.13	118.75	120.05	157.88	53.73

CONCLUSIONS

Two *ansa*-metallocene catalysts showed different trends with increasing the polymerization temperatures in ethylene polymerization. This trend can be attributed to the type of bridge and geometric parameters in indenyl ligands in these two catalysts. At lower polymerization temperatures, the Me₂Si bridge catalyst shows activities higher than Et bridge catalyst, while at temperatures higher than 50 °C, due to the lower thermal stability of silyle bridge, a decrease in the activity of catalyst and molecular weight of polyethylene was observed. ICP results revealed that the optimum calcination temperature was 450 °C for both supported catalysts. At this temperature, the Al/Zr ratio was at the highest level that could maximize the polymerization activity. The melting temperature of polyethylene (132 °C) confirmed the linear structure of HDPE.

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