

IN SITU SILICA SUPPORTED METALLOCENE CATALYSTS FOR ETHYLENE POLYMERIZATION

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ABSTRACT

Bis(2-R-ind)ZrCl₂ (R: H or phenyl) was supported on different types of silica by in situ impregnation method and used for ethylene polymerization. In this method, the step of catalyst loading on support was eliminated and common alkyl aluminum (triisobutylaluminum, TIBA) cocatalyst was used instead of expensive methyl aluminiumoxane (MAO) cocatalyst in the polymerization. The effect of surface area of silica on the performance of the supported catalysts using three different types of silica including EP12 (390 m²/gr.), PQ3060 (570 m²/gr.) and MCM-41 (1100 m²/gr.) was investigated. The surface area had a more critical role relative to other characteristics of the support in the performance of catalysts. By using MCM-41 as support, the kinetic stability was enhanced. The activity of the supported catalysts was increased by increasing the surface area of silica in the order of MCM-41 > PQ3060 > EP12. The morphology of polymer particles was improved and reactor fouling was eliminated by supporting the catalyst.

Keywords: In Situ Impregnation, Heterogeneous Catalysis, Metallocene, Polyethylene, Silica

INTRODUCTION

Polyolefins are the most widely used polymers and their world consumption exceeded 100 million tons in 2010 [1]. Without any doubt, it can be mentioned that polymerization catalysts play the most vital role in polyolefin industry [2-4]. Among the numerous developments in polyolefin catalysts, the discovery of metallocene catalyst is one of the most crucial ones [5,6]. In the presence of MAO as cocatalyst, these types of catalysts show a considerably high activity; furthermore, their unique control over polymer microstructure and producing new

polymers make them as a promising catalyst for various purposes [7-9].

However, the homogeneous metallocene catalysts have some major drawbacks; the lack of polymer morphology, reactor fouling, incompatibility with new processes, and finally their extreme consumption of expensive MAO as cocatalyst are of main concerns [10-16]. To overcome these problems, different approaches have been used, among which the immobilization of metallocene catalyst on a support has been one of the best solutions [17, 18]. Preserving the advantages of the homogeneous catalyst while the catalyst is anchored to a

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support is the key point which has been focused on in the last decade.

As reported in the literature [6,7,19], the route of anchoring metallocene catalysts and the nature of the support play the key roles in the catalyst activity and final properties of the polymer. There are at least three basic methods for supporting metallocene catalysts which include:

- 1- Supporting the metallocene and then reacting with aluminoxane (direct method);
- 2- Supporting the aluminoxane and then reacting with the metal complex (indirect method);
- 3- Immobilizing metallocene compound on support through covalent tethers [7,11, 20].

To the best of our knowledge, up to now, most of attention has been focused on finding the best supporting methods and procedure conditions [21], while the investigation of the effects of physical characteristics of supports such as surface area, pore size, and pore volume on the performance of supported catalysts forms a very small portion of these works [22-24].

In the present study, the in situ impregnation method was used to immobilize Bis(2-R-ind)ZrCl₂(R: H or Phenyl) on different types of silica. By using this method, the preparation complexities encountered in the traditional methods of supporting metallocene catalysts such as direct method, indirect method, and covalent tethering method can be overcome [25, 26]. In this technique, the step of catalyst loading on support was eliminated and a common alkyl aluminum (TiBA) was used in the polymerization [27,28]. Regarding the nature of this method, the effect of support type on the performance of the immobilized catalyst in ethylene polymerization was further investigated.

EXPERIMENTALS

Materials

Three types of silica including MCM-41, PQ-3060, and EP-12 were used in the current work. Spherical MCM-41 support was synthesized according to Nekoomanesh et al. [29]; PQ-3060 was supplied by PQ Co. and EP-12 was provided by Crossfield Co. Methylaluminumoxane (MAO) in toluene (10 wt.%) and triisobutylaluminum (TiBA) were supplied from Aldrich. Bis(2-R-ind)ZrCl₂(R: H or Phenyl) was synthesized according to the procedure reported elsewhere [30]. Toluene and heptane were dried over CaCl₂ by distillation. All the manipulation involving air and/or water sensitive compounds were performed under the atmosphere of dried N₂ in a glove box.

Support Treatment

Table 1 shows the physical properties of the three types of silica employed. As seen in Figure 1 and Table 1, the MCM-41 particles were in a nano range with a high surface area, while the size of EP12 and PQ particles was in the order of micrometer. In addition, the images of supports revealed that the PQ-3060 and MCM-41 particles had a spherical shape, while the morphology of EP-12 was irregular. For the preparation of silica pretreated with MAO, first 5 grams of silica was calcinated under the atmosphere of N₂ at 250 °C for 5 hours. Then, 1 gram of the dehydroxylated silica was suspended in toluene. Afterwards, 4 ml of MAO (10 wt.% in toluene) was added to the suspension and stirred over night. Finally, the silica was washed with toluene and heptane four times and the final suspension was used as the support in the polymerization step.

Polymerization

Ethylene homopolymerization was carried out in a 1-liter Buchi reactor (Buchiglauster bmd 300) equipped with fully controlled systems of temp-

erature, stirring speed, reaction pressure, and mass flow of monomer. *n*-Heptane was introduced into the reactor (400 ml) and was saturated with ethylene at the reaction temperature. TiBA (as a scavenger), MAO-modified silica, and the catalyst solutions were added respectively. At the end of the polymerization (mainly after 30 min), the content of the reactor was poured into an excess amount of methanol, followed by filtering and drying overnight.

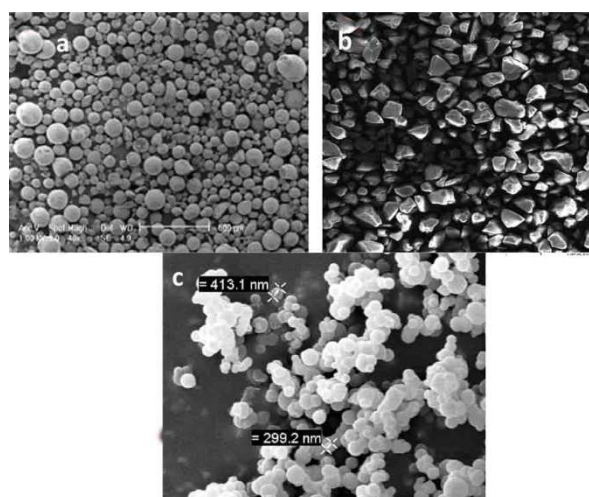


Figure 1: SEM images of the supports; (a) PQ-3060 (magnification of 40X); (b) EP-12 (magnification of 100X); (c) MCM-41 (magnification of 2000X).

Table 1: Textural properties of the supports

Silica	Surface area ($\text{m}^2 \cdot \text{gr}^{-1}$)	Pore volume ($\text{cm}^3 \cdot \text{gr}^{-1}$)	Pore diameter (nm)
EP12	390	1.75	18
PQ3060	570	3.00	21
MCM-41	1100	0.50	2

Characterization

For measuring the surface area of the silica samples, they were outgassed (10^{-2} mbar) at 80 °C for at least 8 hrs. Adsorption-desorption nitrogen isotherms were recorded at -196 °C in a Gemini 2375 (Micromeritics, Norcross, U.S.A.). Specific surface areas were determined by the Brunauer-Emmett-Teller equation ($P/P_0=0.05-0.35$), while the pore volumes and pore diameters were determined with the Barrett Joyner Halenda (BJH) method. The melting point of the

polymer was measured using DSC PL (model STA 780) and Al concentration was measured by inductively coupled plasma (ICP) (model 735-ES Varian Co.). Finally, the morphologies of the supports and polyethylene samples were monitored by a scanning electron microscope (VEGA EMITECH K450X, Czech Republic) after coating the samples with a thin layer of gold.

RESULTS AND DISCUSSION

Effect of Polymerization Conditions on the Performance of Bis(2-R-ind)ZrCl₂ (R: H or, Phenyl) /SiO₂ (PQ 3060)

The results presented in Table 2 show the dependence of polymerization behavior on reaction temperature and monomer concentration. The low activities at temperatures above 60 °C can be attributed to the increase of deactivation rate constants and, consequently, the deactivation of active sites probably by changing their structure [31, 32]. A higher catalyst activity was obtained at higher monomer pressures; it can be stated that by increasing the polymerization pressure the monomer concentration increased in the reaction medium, which led to a rise in the productivity of the system [33-35]. These results also indicate that the activities of the supported catalysts are lower compared to homogeneous counterparts with a reduction of MAO consumption.

Figures 2 and 3 show the effect of polymerization temperature and ethylene pressure on polymerization rate respectively. As seen, the kinetics of the supported catalysts are still of the decay type, which is reflected in the decay index ($DI > 1$) results (Table 2).

However, the convergence of DI values toward unity, in comparison to homogeneous catalysts, confirms the increased catalyst stability. This improvement can be attributed to the elimination of bimolecular deactivation by supporting the catalyst [36,37].

Table 2: Ethylene polymerizations using PQ-3060 silica supported catalyst

	Type of catalyst ^a	Catalyst (mol)	[Al] _{MAO} : [Zr]	Pressure (bar)	T _p (°C)	Activity (kg PE/(mol Zr.hr))	DI ^b
1	A	3×10 ⁻⁶	400:1	4	50	5867	3.0
2	A	3×10 ⁻⁶	400:1	4	60	7333	2.3
3	A	3×10 ⁻⁶	400:1	4	70	6533	2.7
4	A	3×10 ⁻⁶	400:1	4	80	4333	2.5
5	A	3×10 ⁻⁶	400:1	6	60	10667	2.7
6	A _o	1×10 ⁻⁶	5000:1	6	60	40000	8.6
7	B	6×10 ⁻⁶	400:1	6	60	2700	3.3
8	B	6×10 ⁻⁶	400:1	6	70	3033	-
9	B	6×10 ⁻⁶	400:1	6	80	1833	-
10	B _o	3×10 ⁻⁶	2333:1	6	60	10800	10

Polymerization conditions: time= 30 min; n-heptane=400 ml; [TiBA]=1.5 mmol (as a scavenger).

^a Type A: BisIndZrCl₂/SiO₂ (PQ), A_o: the homogenous form of A, type B: Bis2PhIndZrCl₂/SiO₂ (PQ), B_o: the homogenous form of B.

^b DI: decay index: R_p at maximum/ R_p at the end of reaction ($DI = R_{p(\text{maximum})}/R_{p(30 \text{ min})}$)

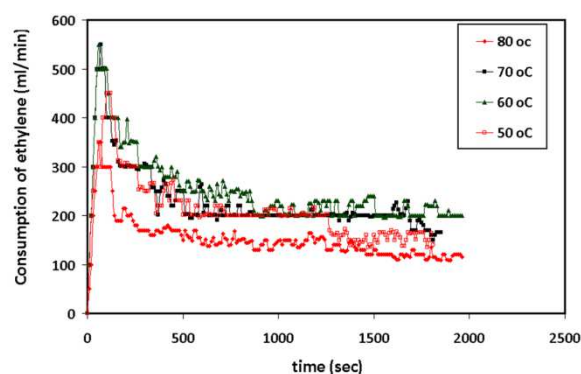


Figure 2: Kinetic profiles of ethylene polymerization with BisIndZrCl₂/Silica (PQ-3060) showing the effect of polymerization temperature

The morphology of polymer particles depicted in Figure 4 shows that the supported catalyst produces spherical polymer particles, replicating the initial shape of support particles; this is in accordance with the replication phenomenon and no evidence of reactor fouling can be found [21,38,39]. In contrast, the shape of the polymer produced by the homogeneous catalyst was completely irregular.

Effect of Polymerization Conditions on the Performance of Bis(2-R-ind)ZrCl₂ (R: H or Phenyl)/SiO₂ (MCM-41)

The polymerization results tabulated in Table 3

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clearly indicate the improvement achieved in the performance of the immobilized catalyst by using MCM-41 as a support.

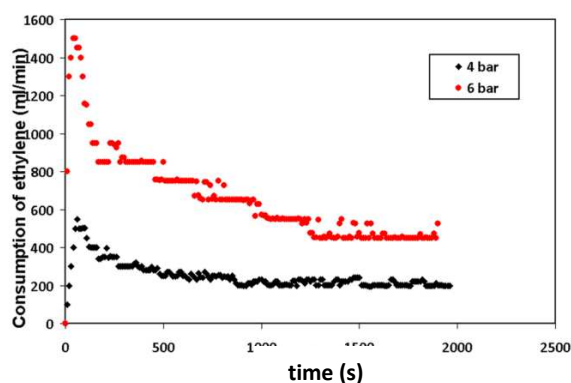


Figure 3: Kinetic profiles of ethylene polymerization with BisIndZrCl₂/Silica (PQ-3060) showing the effect of monomer pressure

DI values show that the catalyst supported on MCM-41 is stabler than the one supported on PQ3060. In other words, by changing the type of the support, the kinetic curves were shifted from decay type to stable type. However, the morphology of polymer particle was irregular, which was probably due to the nano size of the support particles causing polymer particles to agglomerate [29].

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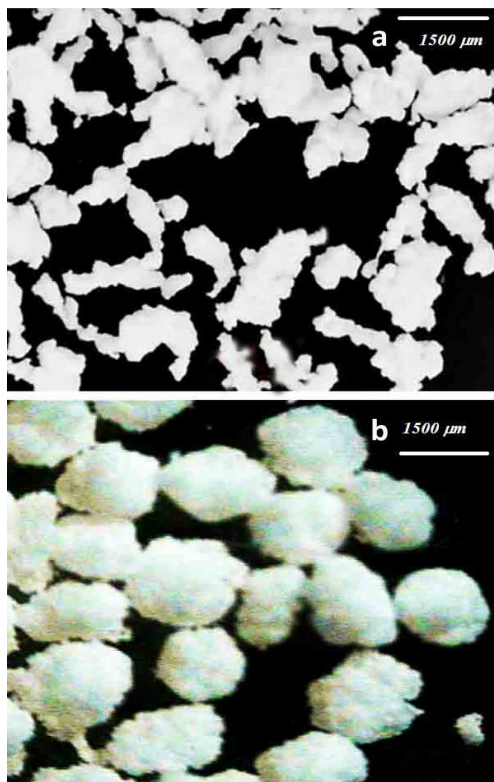


Figure 4: Morphology of polymer particles synthesized by (a) BisIndZrCl₂ homogenous form and (b) BisIndZrCl₂/Silica (PQ-3060)

Nevertheless, the observed spherical floccules in Figure 5 prove that the replication phenomenon

has definitely occurred. The activity of the substituted indenyl based supported catalyst ($\sim 3000 \text{ kg PE.mol Zr}^{-1}.\text{hr}^{-1}$) is less than BisIndZrCl₂ ($\sim 10000 \text{ kg PE.mol Zr}^{-1}.\text{hr}^{-1}$), which can be attributed to electronic and steric effects of the substituents on the performance of the catalyst [40].

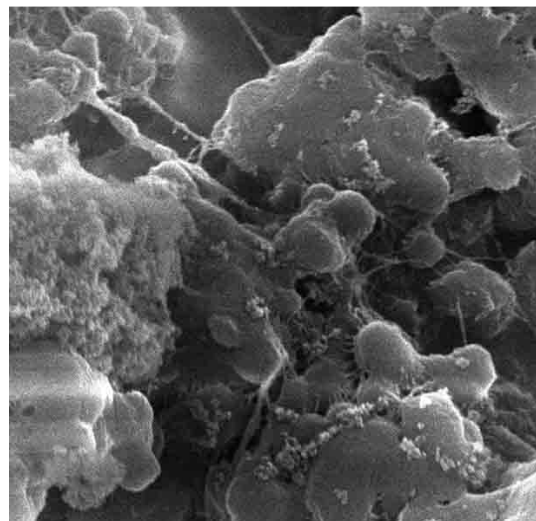


Figure 5: Morphology of polymer particles synthesized by BisIndZrCl₂/Silica (MCM-41). (Magnification of 2000X)

Table 3: Ethylene polymerizations using MCM-41 supported catalyst

	Type of Catalyst ^a	Catalyst (mol)	[Al] _{MAO} : [Zr]	Pressure (bar)	T _p (°C)	Activity (kg PE/(mol Zr.hr))	DI ^b
1	C	5×10 ⁻⁶	240	4	60	7280	1.2
2	C	5×10 ⁻⁶	240	4	70	8520	-
3	C	1×10 ⁻⁵	120	6	60	11300	1
4	A ₀	1×10 ⁻⁶	5000	6	60	40000	8.6
5	D	1×10 ⁻⁵	120	6	50	700	-
6	D	1×10 ⁻⁵	120	6	60	1300	1.8
7	D	1×10 ⁻⁵	120	6	70	860	-
8	B ₀	3×10 ⁻⁶	2333	6	60	10800	10

Polymerization conditions: time=30 min; Heptane=400 ml; [TiBA]=1.5 mmol (as a scavenger);

^a Type C: BisIndZrCl₂/SiO₂ (MCM), A₀: the homogenous form of C, type D: Bis2PhIndZrCl₂/SiO₂ (MCM), B₀: the homogenous form of D.

^b DI: decay index: R_p at maximum/ R_p at the end of reaction ($DI = R_{p\text{maximum}}/R_{p30\text{min}}$)

Effect of the Surface Area of Support

The Al content of the modified supports, determined by ICP (Table 4), clearly showed that increasing MAO concentration increased the

amount of grafted Al. It was observed that MCM-41 with a specific surface area above 1000 m².gr⁻¹ was more capable of hosting Al. It is obvious that by increasing the surface area, the accessibility of OH groups of the support rises

and, consequently, the probability of loading Al is enhanced.

Table 4: Al contents determined by ICP

Type of Support	Initial Aluminum (mmol.gr. silica ⁻¹)	Loaded Al (wt.%)
PQ-3060	3	--
PQ-3060	6	9.1
PQ-3060	12	12.2
MCM-41	3	5.2
MCM-41	6	9.5
MCM-41	12	13.6

Table 5 shows that the surface area can play a key role in the performance of the catalyst. It was observed that when the surface area of the catalyst was increased, the activity of catalyst was raised too, since it increased the probability of contact between active centers and supported MAO [41]. Undoubtedly, the higher

stability of the kinetic profile of the catalyst supported on MCM-41 (Figure 6) can be related to the better accessibility of the active centers during polymerization. It seems that in the in situ supported catalysts new catalytic sites are continuously formed on the external surface of the silica particles by the absorption of the catalyst compounds which are available in the liquid phase during polymerization [42]. The studies of Soga [43] and Wanke [24, 44] have confirmed the dominant role of the pore volume of support on catalyst activity, whereas the effect of surface area has not been taken into account. The importance of the surface area becomes more dominant in the in situ impregnation method in comparison to the traditional techniques, since the contact time between the catalyst species and activated support drastically decreases.

Table 5: Effect of surface area on the performance of BisIndZrCl₂ catalyst in ethylene polymerization

Type of support	Surface area (m ² .gr. ⁻¹)	Activity(kg PE.(mol Zr.hr) ⁻¹)	T _m (°C)	Crystallinity (%)
EP-12	350	1700	136.5	---
PQ-3060	570	5700	138.1	51.2
MCM-41	1100	11300	140.4	55

Polymerization conditions: Heptane=400 ml; [Al]_{TIBA}=2 mmol (as a scavenger); P=6 bar; [Al]_{MAO}/[Zr]=120:1; [Zr]=1×10⁻⁵ mol

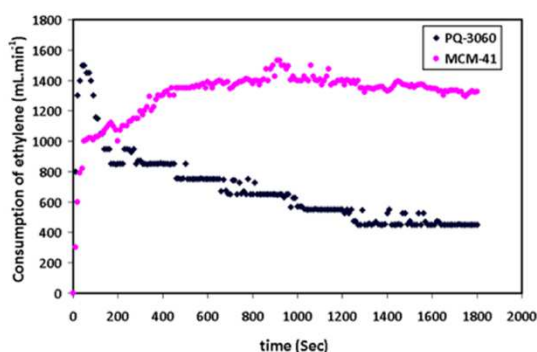


Figure 6: Effect of the type of support on the kinetic profiles in the polymerization of ethylene

CONCLUSIONS

The effects of polymerization conditions and support specifications on Indenyl-based supported metallocene catalysts were investigated. The BisIndZrCl₂/SiO₂ (PQ) supported catalyst showed

the highest activity (~10000 kg PE/(mol Zr.hr)) at 60 °C and 6 bar. The catalyst with substituted indenyl ligand (2- phenyl indenyl) showed a lower activity (~3000 kg PE/(mol Zr.hr.)) than its non-substituted counterpart. The morphology of polymer particles was improved and reactor fouling was eliminated by supporting the catalyst. It was observed that the consumption of MAO was decreased by supporting the catalyst; the ratio of Al to Zr ([Al]:[Zr]) decreased from 5000 to lower than 500. The activity of BisIndZrCl₂ catalyst supported by the in situ impregnation method was investigated using three types of supports. The BisIndZrCl₂/MCM-41 showed the highest activity, which was twice as large as the PQ-3060 and EP-12 supported catalysts. MCM-41 support by the

surface area of $1100 \text{ m}^2 \cdot \text{gr}^{-1}$ showed a catalyst activity of 11.3 (kg PE/(mol Zr.hr)), while the micro-sized supports, namely PQ-3060 and EP-12, with the respective surface area of 590 and $390 \text{ m}^2 \cdot \text{gr}^{-1}$ showed a catalyst activity of 5.6 and 1.7 (kg PE/(mol Zr.hr)) respectively. It was confirmed that the surface area of the support had the most crucial effect on the performance of the in situ supported catalysts. This behavior can be attributed to the decreased contact time during catalyst impregnation in this method, which amplifies the importance of the probability of the contact between catalyst compounds and the exterior potential impregnation sites.

NOMENCLATURE

BJH	Barett Joyner Halenda
BisIndZrCl ₂	Bis(indenyl)zirconiumdichloride
Bis2PhIndZrCl ₂	Bis(2-phenyl indenyl)zirconium dichloride
DI	Decay index
ICP	Inductively coupled plasma
MAO	Methyl aluminiumoxane
TiBA	Triisobutylaluminum

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