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# Effect of Mn doped-titania on the activity of metallocene catalyst by in situ ethylene polymerization

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ABSTRACT

Ethylene polymerization was carried out using highly active metallocene catalysts ($Cp_2ZrCl_2$ and $Cp_2TiCl_2$) in combination with methylalumoxane. Titanium(IV) oxide containing 1% Mn as dopant was used as nanofillers. The influence of filler concentration, reaction temperature and pressure on the catalytic activity and polymer properties was investigated. There was a fourfold increase in the activity of zirconocene catalyst by addition of doped-titania. The morphology indicates that the doped-titania nanoparticles have a nucleus effect on the polymerization and caused a homogeneous PE shell around them. The optimum condition for polymerization was found to be 30 °C.

## 1. Introduction

Ethylene polymerization is carried out using various techniques such as free-radical polymerization, Phillips catalyst, Zeigler-Natta catalyst, metallocene catalyst and post-metallocene catalyst [1–3]. The metallocene catalysts offer a better flexibility and versatility for the synthesis and control of polyolefin structure in comparison to other olefin polymerization catalysts [4]. Initially, the metallocene catalyst showed less activity in the presence of different alkylaluminum cocatalyst subsequently it was found that there was a remarkable increase in activity by adding small amounts of water to the system [5]. An enormous increase in activity was found when methyl aluminoxane (MAO) was used with titanocenes and zirconocenes [6,7]. Metallocene/methylaluminoxane catalysts are highly active for the production of precisely designed polyolefins [8–12] and permit the control of the molecular weights. However, the main drawback in the case of metallocene catalyst is the extremely high molar Al-to-transition metal ratio to achieve the high activity, which to some extent may impair the value of the catalyst system in commercial application [12,13].

The cationic metallocene compounds do not need any cocatalyst for polymerization [14–16]. By supporting catalysts or co-catalysts on inorganic compounds ($Al_2O_3$, $SiO_2$, and $MgCl_2$) [14,17–19] or polymeric materials [14,18,19], the amount of methylaluminoxane that is needed to enrich the activity of supported catalysts was reduced [16,18,19]. It was found that the activity of the homogeneous system was higher compared to the heterogeneous one, which demanded support modification in order to maintain the activity. $TiO_2$–$SiO_2$ mixed oxide has been considered to be very attractive as combined catalyst and support, which have attracted much attention in recent years. It was reported that $TiO_2$–$SiO_2$ mixed materials have been used as catalysts and supports for various reactions [20,21].

In the recent past, efforts to utilize $TiO_2$ to enhance catalytic activity and overall polymer properties have gained a major momentum. The three primary methods employed to synthesize $TiO_2$ filled polymers are melt compounding [22–26], solution mixing [27] and in situ polymerization [28–30]. The in situ polymerization seems to be more promising compared to the other methods as it leads to homogeneous dispersion of the filler in the polymer matrix. It was reported that the anatase form of $TiO_2$ enhances the activity of zirconocene catalyst whereas the rutile form of $TiO_2$ was found to be detrimental to the activity of the catalyst [31]. A recent study also showed that the modified methylaluminoxane (MMAO)/$TiO_2$ (anatase) exhibited about four times higher intrinsic activity based on MMAO than the MMAO/$TiO_2$ (rutile) [32].

Progress made in the development of nanotechnology has rendered it possible to enhance $TiO_2$ effectiveness by modifying its surface with noble metal deposition. The purpose of doping $TiO_2$

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nanoparticles with metals is to create a heterojunction [33]. The applications for doped $TiO_2$ nanocomposites range from antimicrobial coatings on textiles, the inactivation of endospores, solid-surface antimicrobial coatings, and aqueous system-based biocides [34–36]. In this study, we have used titanium dioxide doped with manganese to investigate the effect of filler on catalytic activity in polymerization, particle growth and characteristics of the resulting polymers.

## 2. Experimental methods

### 2.1. Materials

All manipulations were carried out under $N_2$ using standard Schlenk and glove box techniques. Titanium(IV) oxide containing 1% Mn as dopant, nanopowder (<100 nm) ($TiO_2$/Mn), $Cp_2ZrCl_2$, $Cp_2TiCl_2$ and all other chemicals were purchased from Aldrich Chemicals and used without further purification. Solvents were purified by standard techniques. The TiO2 used has an anatase phase composition with a surface area >14.0 $m^2$/g.

### 2.2. Characterization

Scanning electron microscope (SEM) was taken by HITACHI S-4200. Transmission electron microscope images were taken by JEOL, JEM 2011 (for high resolution TEM) and HITACHI H-7600. Molecular weight of PE was determined by High Temperature-Gel Permeation Chromatography using 1,2,4-trichlorobenzene as a solvent.

Crystallinity analysis of PE were determined by crystallization analysis fractionation (CRYSTAF) (Polymer Char, Spain) using an IR detector in 1,2,4-trichlorobenzene. Crystallization was carried out in stainless-steel stirred vessels of 50-mL volume. Five crystallization vessels were installed in the main oven (a gas chromatography oven) and attached via a rotary valve to a dual-channel optoelectronic IR detector (with 3.5 μm as the measurement wavelength). Crystallization rate of 0.2 °C/min was used for the analysis. The IR cell was kept heated isothermally during the whole experiment at 150 °C.

### 2.3. Polymerization

#### 2.3.1. Synthesis of PE/doped $TiO_2$ nanocomposites at low pressure

Ethylene polymerization was performed in a 250 mL round-bottom flask equipped with a magnetic stirrer and a thermometer. The catalyst and required amount of $TiO_2$/Mn were added to the flask and the reactor was charged with toluene (80 mL). The reactor was immersed in a constant temperature bath previously set to desired temperature (30 °C and 60 °C). When the reactor temperature had been equilibrated to the bath temperature, ethylene was introduced into the reactor after removing nitrogen gas under vacuum. When no more absorption of ethylene into toluene was observed, the cocatalyst was injected into the reactor and then the polymerization was started. Polymerization was quenched by the addition of methanol containing HCl (5 vol.%) and then the unreacted monomer was vented. The polymer was washed with an excess amount of methanol and dried in vacuum at 50 °C. To make a worthy comparison all data were collected under similar conditions.

#### 2.3.2. Synthesis of PE/doped $TiO_2$ nanocomposites at high pressure

The polymerization was carried out in a 1-L autoclave reactor operated in a semi-batch mode. The reactor was carefully cleaned and dried under vacuum at 150 °C for 3 h, and allowed to cool under nitrogen. Purified toluene was transferred to the reactor under nitrogen pressure through a transfer needle. The mixture was kept under stirring while the reactor was heated up to the desired polymerization temperature (30 °C). Once the desired temperature was established, prescribed amount of catalyst, co-catalyst and filler solution or slurry were added to the reactor under nitrogen atmosphere using gas-tight syringes. To start polymerization, the reactor was pressurized by ethylene to the desired pressure. The reactor was kept at constant pressure by continuous feeding of gaseous ethylene to the reactor. The reactor temperature was maintained within ±l °C of desired temperature by cooling circulation. The reaction was stopped by rapid depressurization of the reactor followed by quenching with methanol. The polymer was washed with an excess amount of methanol and dried in vacuum at 50 °C. All the data were collected by maintaining similar conditions in order to compare the results.

## 3. Results and discussion

### 3.1. Effect of filler concentration on the activity of the catalyst and polymer properties

The polyethylene nano-composites were synthesized by in situ polymerization using nanofillers. Table 1 summarizes the results of the polymerization activity and polymer characteristics.

The polymerization activity was found to increase with increase in the concentration of nanofillers and the maximum polymerization activity of 431 × $10^3$ gPE/mol Zr h bar was obtained using a filler concentration of 15 mg (Entry 3, Table 1).

It is evident from Table 1 that nanotitanium oxide doped with manganese enhances the ethylene polymerization activity. Furthermore, polymerization runs with titania and manganese as fillers showed a marked decrease in the polymerization activity compared to nanotitanium oxide doped with manganese (15 mg filler incorporated) under the same reaction conditions as shown in Table 1. It is thus apparent that titanium doped with manganese plays a vital role in the polymerization reaction by enhancing the activity of the catalyst which is believed to be due to the intrinsic activity of the active species present on the doped titania [31].

It has been reported previously that change of metal centre in the catalyst structure can have remarkable effects on polymer

**Table 1**
Ethylene polymerization results at 1.3 bar.[a]

| Entry no. | Catalyst/Filler (in mg) | Activity[h] | $T_m$[i] (°C) | $X_c$[i] (%) | Mn (g/mol) |
|---|---|---|---|---|---|
| 1 | Zr/0[b] | 152 | 133 | 78 | 74,400 |
| 2 | Zr/10 | 181 | 131 | 76 | 87,200 |
| 3 | Zr/15 | 431 | 130 | 80 | 37,600 |
| 4 | Zr/20 | 171 | 131 | 74 | n.d.[j] |
| 5 | Zr/15[c] | 121 | 135 | 76 | 93,600 |
| 6 | Zr/15[d] | 153 | 134 | 73 | 102,400 |
| 7 | Zr/15[e] | 364 | 131 | 75 | 83,200 |
| 8 | Zr/15[f] | 328 | 132 | 75 | n.d. |
| 9 | Zr/0[g] | 281 | 131 | 68 | n.d. |
| 10 | Zr/1[g] | 255 | 125 | 74 | n.d. |
| 11 | Ti/0 | 76 | 134 | 78 | n.d. |
| 12 | Ti/15 | 155 | 135 | 58 | n.d. |
| 13 | Ti/0[g] | 141 | 134 | 69 | n.d. |
| 14 | Ti/15[g] | 115 | 134 | 61 | n.d. |

[a] Polymerization conditions: solvent toluene = 80 mL, temp = 30 °C, time = 30 min, catalyst (Zr = $Cp_2ZrCl_2$, Ti = $Cp_2TiCl_2$) amount = 20.5 μmol, filler is Mn (1%) dopped $TiO_2$, [Al]/[M] = 700.
[b] Control.
[c] Pure $TiO_2$.
[d] Pure Mn.
[e] Reaction time = 60 min.
[f] Reaction time = 120 min.
[g] Reaction temp = 60 °C.
[h] $\times 10^{-3}$ gPE/mol h bar.
[i] Determined by DSC measurements.
[j] Not determined.