

# Supported $\text{SiO}_2$ - ${}^n\text{BuSnCl}_3$ /MAO/ $({}^n\text{BuCp})_2\text{ZrCl}_2$ Catalyzing MAO Cocatalyst-Free Ethylene Polymerization: Study of Hydrogen Responsiveness

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**ABSTRACT:** A supported metallocene catalyst was synthesized by sequentially loading methylaluminoxane (MAO) (30 wt % in toluene) and  $({}^n\text{BuCp})_2\text{ZrCl}_2$  on partially dehydroxylated silica ES 70 modified by  ${}^n\text{BuSnCl}_3$ . Its shock load hydrogen responsiveness was evaluated by polymerizing ethylene for 1 h at 8.5 bar (g) and 75°C without separately feeding the MAO cocatalyst. The shock load hydrogen feeding increased the ethylene consumption (at a fairly constant rate), catalyst productivity, as well as the resin bulk density and average particle size at  $\Delta P$  (of hydrogen)  $\geq 3.0$  psi. The bulk density increased from 0.25 to 0.31 g/cm<sup>3</sup>. This shows a procedure for overcoming the inherent drop in catalyst productivity caused by heterogenization of metallocenes (that is a method for catalyst activation) and improving the resulting resin bulk density. The volume-weighted

mean particle diameter of the resulting polyethylenes was found to be 5.80–11.12-fold that of the catalyst corresponding to  $\Delta P = 0.00$ –7.11 psi, respectively. The resulting kinetic profiles showed to be fairly stable. However,  $M_w$  and polydispersity index were not affected. The particle size distribution, average particle size, and the scanning electron microscope photographs of the resulting resin particles confirmed the occurrence of the replication phenomenon. On the basis of the above findings, the mechanism of ethylene polymerization under the present experimental conditions has been revisited. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3149–3157, 2007

**Key words:** supported zirconocene catalysts; silica functionalization; replication phenomenon; hydrogen responsiveness; particle size distribution; bulk density

## INTRODUCTION

Metallocenes belong to the family of single-site catalysts. Hence, they produce narrow molecular weight distribution polyolefins; the polydispersity index (PDI) is typically restricted between 2 and 3.<sup>1–5</sup> Such a narrow PDI is a matter of concern, especially from the processing viewpoint. Therefore, hydrogen responsiveness of metallocene catalyst is a subject of growing investigation. A number of studies have been devoted to study how hydrogen, the traditional chain transfer agent in olefin polymerization, affects the PDI and average molecular weights of metallocene-based polyolefins. What follows reviews only those studies that particularly use supported metal-

locenes and the separately fed methylaluminoxane (MAO) cocatalyst in slurry ethylene polymerization.<sup>6–10</sup>

Kim et al.<sup>6</sup> studied the hydrogen responsiveness of the following three supported catalysts— $\text{SiO}_2$ /MAO/Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>,  $\text{SiO}_2$ /MAO/Cp<sub>2</sub>HfCl<sub>2</sub>, and  $\text{SiO}_2$ /MAO/Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>/Cp<sub>2</sub>HfCl<sub>2</sub>—with respect to ethylene polymerization. The objective was to compare the performance of the bimetallic catalyst with that of the individual analogs. Hydrogen was fed into the reactor in the form of shock load. The peak molecular weight of the polyethylenes resulting from Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> did not change, whereas that due to Cp<sub>2</sub>HfCl<sub>2</sub> decreased fairly linear with increasing hydrogen shock load. Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> and Cp<sub>2</sub>HfCl<sub>2</sub>, both produced, with and without hydrogen, monomodal molecular weight distribution polyethylenes. On the contrary, the bimetallic catalyst produced narrow to broad and bimodal polyethylenes (2.78 ≤ PDI ≤ 4.13) under similar polymerization conditions. The influence of hydrogen on the catalyst activity/productivity was not reported.

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Blom and Dahl<sup>7</sup> compared the hydrogen responsiveness of SiO<sub>2</sub>/MAO/Cp<sub>2</sub>ZrCl<sub>2</sub> and SiO<sub>2</sub>/MAO/Cp\*<sub>2</sub>ZrCl<sub>2</sub> with that of one commercial Phillips catalyst (SiO<sub>2</sub>/CrO) and one Union Carbide catalyst (SiO<sub>2</sub>/Cp<sub>2</sub>Cr). They added 2.0 bar (g) of hydrogen at the beginning of ethylene polymerization. The polymerization pressure and temperature were 38 bar (g) and 80°C, respectively. The rate of consumption of hydrogen by these catalysts varied as follows: Cp\*<sub>2</sub>ZrCl<sub>2</sub> > Cp<sub>2</sub>ZrCl<sub>2</sub> [dmt] Cp<sub>2</sub>Cr [tmt] CrO (low sensitivity). Cp\*<sub>2</sub>ZrCl<sub>2</sub> produced much higher weight average molecular weight (*M<sub>w</sub>*) and broader PDI than Cp<sub>2</sub>ZrCl<sub>2</sub>. The *M<sub>w</sub>* and PDI in the first case were 190,000 g/gmol and 44, respectively, whereas those in the second case were 9400 g/gmol and 8.9, respectively. When hydrogen was fed at several constant flow rates, Cp\*<sub>2</sub>ZrCl<sub>2</sub>, unlike Cp<sub>2</sub>ZrCl<sub>2</sub>, produced bimodal molecular weight distribution products, in addition to the broad molecular distribution ones.

Chu et al.<sup>8,9</sup> used *in situ* supported Cp<sub>2</sub>ZrCl<sub>2</sub> and Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>. *In situ* supporting means contacting the metallocene with MAO-loaded silica during polymerization in the reactor. The influence of hydrogen on ethylene polymerization activity varied with the metallocene structure. For Cp<sub>2</sub>ZrCl<sub>2</sub>, the polymerization activity increased as the hydrogen partial pressure was increased from 0 to 60 psi(g). For Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, the polymerization activity initially increased; then, it decreased with further increase in the hydrogen partial pressure. In either case, hydrogen drastically decreased the peak molecular weight. Also, the molecular weight distribution turned from monomodal to bimodal and broad. Köppl and Alt<sup>10</sup> also found that hydrogen, for 9-fluorenylidene-1-cyclopentadienyldiene-2-hex-5-enylidene supported on silica gel, modified with partially hydrolyzed trimethylaluminum, broadened the molecular weight distribution of the resulting polyethylenes.

The above hydrogen responsiveness studies were conducted particularly in the presence of the MAO cocatalyst. Note that an MAO-cocatalyzed ethylene polymerization process has several limitations that include catalyst leaching, reactor fouling, and very low bulk density resin. Other disadvantages are gelling of MAO and variations in its quality from one production batch to another. Also, the occurrence of competitive diffusion between ethylene and the separately fed MAO adds to the aliased factorial interactions. Hence, MAO cocatalyst-free polymerization is industrially desirable to achieve better resin bulk density, decrease the production cost, and overcome the aforementioned problems.<sup>11–14</sup> To the best of our knowledge, the hydrogen responsiveness of a supported metallocene catalyst, using MAO cocatalyst-free ethylene polymerization, has not yet been reported in the literature. Therefore, the present

study investigates the hydrogen responsiveness of the supported catalyst [Silica ES 70-<sup>n</sup>BuSnCl<sub>3</sub>/MAO/(<sup>n</sup>BuCp)<sub>2</sub>ZrCl<sub>2</sub>] by polymerizing ethylene without separately feeding the MAO cocatalyst. We have chosen (<sup>n</sup>BuCp)<sub>2</sub>ZrCl<sub>2</sub> because it is one of the preferred catalysts for ethylene homopolymerization.<sup>15–23</sup> It is reasonably cheaper than most of the metallocene analogs. It shows exceedingly high activity in solution ethylene polymerization in presence of MAO cocatalyst. <sup>n</sup>BuSnCl<sub>3</sub> has been selected because this has shown to act as a novel spacer compound.<sup>24</sup>

## EXPERIMENTAL

### Materials

Silica ES 70 (from Crosfield), having surface area of 300 m<sup>2</sup>/g, an average pore volume of 1.6 mL/g and particle size of 35 μm, and a pore size of 195 Å, was used as the support.

(<sup>n</sup>BuCp)<sub>2</sub>ZrCl<sub>2</sub> and MAO (30 wt % in toluene) were purchased from Chemtura. The following chemicals—HCl, HF, H<sub>3</sub>BO<sub>3</sub>, Al(NO<sub>3</sub>)<sub>3</sub> stock solution in dilute HNO<sub>3</sub> (1.0 × 10<sup>3</sup> mg Al/L), ammoniumhexafluorosilicate (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> (1.0 × 10<sup>3</sup> mg Si/L), AlCl<sub>3</sub>, and ZrCl<sub>4</sub> stock solution (1.0 × 10<sup>3</sup> mg Zr/L)—used for determining the elemental composition of the synthesized catalysts, were obtained from BDH.

Analytical grade toluene, *n*-hexane (both 99.999% pure), molecular sieves, 0.05 (w/v)% 2,6-di-*tert*-butyl-4-methyl phenol (BHT), and 1,2,4 trichlorobenzene (TCB)—all were obtained from Aldrich. <sup>n</sup>BuSnCl<sub>3</sub> was bought from Gellest Chemicals, USA. Acetylene, ethylene, hydrogen, and nitrous oxide (99.999% pure) were procured from Abdullah Hasim, a local vendor.

### Catalyst synthesis

All the manipulations were done under an inert atmosphere of argon using standard Schlenk technique. The solvents used were dried using 4A type molecular sieve.

The required amount of silica was dehydroxylated at 800°C for 4 h using a Thermcraft furnace equipped with a vertical quartz glass tube, a digital temperature indicator and controller, a gas flow meter, and a vacuum pump. The silica was continuously fluidized using nitrogen. Upon dehydroxylation, it was stored in an inert glove box.

The dehydroxylated silica was functionalized using <sup>n</sup>BuSnCl<sub>3</sub> as follows. The required amount of silica was placed in a 250 mL Schlenk flask under argon. Then it was slurried with 70.0 mL of dry toluene under continuous magnetic stirring; 1.30 g of <sup>n</sup>BuSnCl<sub>3</sub> was injected into the silica-toluene slurry.

The resulting mixture was refluxed at 130°C for 24 h. The final solid product was filtered, washed thrice with 30.0 mL of toluene, thrice with 20.0 mL of *n*-pentane, and dried for several hours under high vacuum. What follows summarizes the synthesis of the final catalyst.

The above-functionalized silica (3.0747 g) was placed in a catalyst synthesis reactor which has been detailed elsewhere.<sup>25</sup> The functionalized silica was slurried by adding 20.0 mL of dry toluene to it. Then 9.8 mL of the as-received 30 wt % MAO was slowly added to the above slurry at room temperature and was continuously stirred for 60 min. Hence, the 30 wt % MAO makes an integral component of the supported catalyst.

Next (<sup>187</sup>BuCp)<sub>2</sub>ZrCl<sub>2</sub> (0.2460 g) was separately placed in a Schlenk flask and was dissolved in 15.4 mL of dry toluene. This (<sup>187</sup>BuCp)<sub>2</sub>ZrCl<sub>2</sub> solution was injected into the reactor and was again stirred continuously for 60 min. Following this, the final catalyst was dried under high vacuum at 55°C for several hours.

#### Determination of catalyst bulk composition

The bulk elemental compositions of the synthesized catalysts (in terms of Al, Si, Sn, and Zr) were determined by atomic absorption (AA) spectroscopy using the Perkin–Elmer equipment *AAAnalyst 100*. The wave lengths of 309.3, 251.6, 235.5, and 360.1 nm represented Al, Si, Sn, and Zr, respectively.<sup>26</sup> High purity nitrous oxide-acetylene flame was used for the analyses. The determination of each element involved two common steps—calibration of the AA spectrometer and preparation of the experimental sample solution. The procedure for determining Al, Si, and Zr, are detailed elsewhere.<sup>25</sup> Therefore, what follows summarizes only the determination of Sn (tin).

The AA spectrometer was calibrated using spectroscopic standard solution (1.0 × 10<sup>3</sup> mg Sn/L from BDH). The experimental sample solution was prepared as follows. About 50.0 mg of the catalyst sample was transferred to a 60 mL teflon bottle having a tight seal cap. Half an milliliter of deionized water, 2.0 mL HF, and 1.0 mL HNO<sub>3</sub> was sequentially added to the catalyst sample. The bottle was tightly closed and heated in a water bath at 70°C for half an hour. After this, the catalyst sample bottle was removed from the water bath and cooled to room temperature. The resulting solution was diluted to 50.0 mL by adding deionized water in a volumetric flask and was used for the analysis of tin.

The synthesized catalyst ES70-BuSnCl<sub>3</sub>/MAO/(<sup>187</sup>BuCp)<sub>2</sub>ZrCl<sub>2</sub> were found to have 0.04 wt % Sn, 0.77 wt % Zr, and 17.8 wt % Al. This offers an Al:Zr molar ratio of 78 in the synthesized catalyst.

#### Polymerization trials

Ethylene was polymerized using a computer-interfaced, Imtech laboratory-scale reactor set up. The details are available elsewhere.<sup>25</sup> The reactor consisted of a fixed top head and a one-liter jacketed Büchi glass autoclave. The polymerization temperature was controlled using a HAAKE F6 heating circulator. Labview 5.1, a real time programming software package, acquired the data and controlled the process variables.

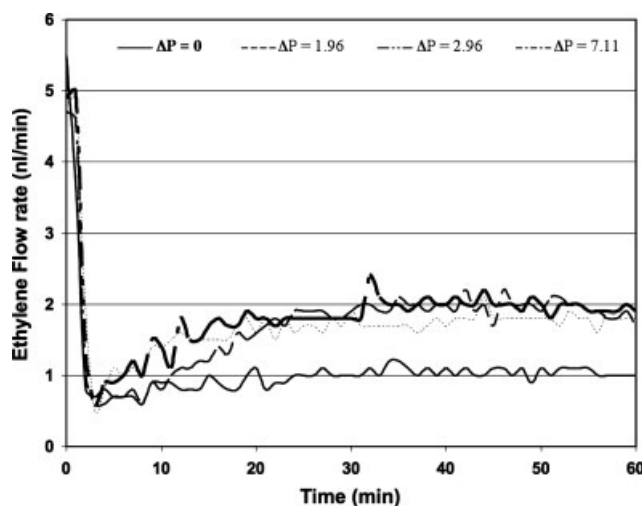
The reactor was baked for an hour at about 120°C. Then it was pressure-purged with nitrogen 4–5 times at about the same temperature. About 450 mL of hexane was transferred to the reactor. The resulting mixture was stirred at 40–50 rpm for 10 min.

The desired amount of the catalyst (30–40 mg as per the Zr loading) was placed in a 250 mL round bottom Schlenk flask in an inert atmosphere glove box. Then it was slurried in the Schlenk flask using 50.0 mL of hexane. One end of a teflon tube provided with a swagelok nut was connected to the reactor feed port. The other end was dipped into the bottom of the catalyst slurry through a rubber septum closing the flask. The catalyst slurry was then transferred into the reactor (under positive pressure of argon) by opening the feed port valve. It was kept in suspension by swirling the flask, and the polymerization diluent (hexane) was stirred at about 100 rpm during this transfer process. After transfer of the catalyst slurry, the feed port valve was closed and the reactor was heated to 75°C.

Feeding the reactor with ethylene to a total pressure of 8.5 bar (g) started the polymerization which was continued for 1 h at 400 rpm. The polymerization was quenched by (a) stopping the ethylene flow, (b) venting the post polymerization ethylene (in the reactor) to the atmosphere, and (c) gradually cooling the reactor to the room temperature by passing coolant through an internal cooling coil. Note that the second action (b), that is, reducing ethylene pressure from 8.5 bar (g) to atmospheric, drastically decreased its solubility in the hexane solvent. Under the present situation, hexane did not contain any separately fed MAO cocatalyst, which could leach the supported catalyst ingredients. Hence, no polymerization occurred in the solvent. Therefore, the addition of acidic methanol was not necessary to quench the reaction. Then, the data acquisition was stopped and the stirrer speed was reduced to about 100 rpm.

Upon completion of the polymerization trials as described earlier, the reactor was immediately opened; the resulting polymer was filtered, dried under ambient conditions in a hood, and weighed.





**Figure 1** Effect of shock load of hydrogen on the kinetic profile of MAO-free ethylene polymerization by the experimental catalyst. Polymerization conditions: pressure = 8.5 bar (g); temperature = 75.0°C; time = 1 h.

The hydrogen responsiveness was studied under shock load as described below. The magnitude of the shock load corresponded to differential change in hydrogen pressure,  $\Delta P = 1.96, 2.96, 3.00,$  and  $7.11$  psi.

From a regular high-pressure cylinder, hydrogen was first transferred to a 100 mL stainless steel cylinder (connected to the reactor top) until the pressure gauge mounted on it read 30 psi (g). Then, a shock load of hydrogen was fed to the reactor from the 100 mL cylinder by allowing the pressure to drop as per the values reported earlier. The reactor was heated to 75°C. Next ethylene was fed into the reactor at 8.5 bar (g). The amount of hydrogen introduced was so small that it did not practically change the overall pressure in the reactor. The rest of the polymerization trials remained as described earlier.

### Polymer characterization

The synthesized polyethylenes were characterized in terms of molecular weight distribution (polydispersity index) and average molecular weight using gel permeation chromatography (GPC). The GPC assay was done at 150°C using Waters Alliance GPC 2000 model. Two mixed bed columns (PLgel 10  $\mu$ m, Polymer Laboratories) were used.

The antioxidant, 0.05 (w/v)% 2,6-di-*tert*-butyl-4-methyl phenol (BHT), was added to 1,2,4 trichlorobenzene (TCB) to prevent the polymer sample from degrading. A sample solution of 0.075–0.100 (w/v)% was prepared at 150°C in this antioxidant-containing solvent. The resulting solution (200  $\mu$ L) was injected into the GPC column. The chromatogram data

were acquired and analyzed using the Millenium 32 software.

The equipment was calibrated using polystyrene standards. The polystyrene-based calibration curve was converted into the universal one using the Mark-Houwink constants (values) of polystyrene ( $K = 0.000121$  dL/g and  $\alpha = 0.707$ ) and polyethylene ( $K = 0.000406$  dL/g and  $\alpha = 0.725$ ).<sup>27</sup>

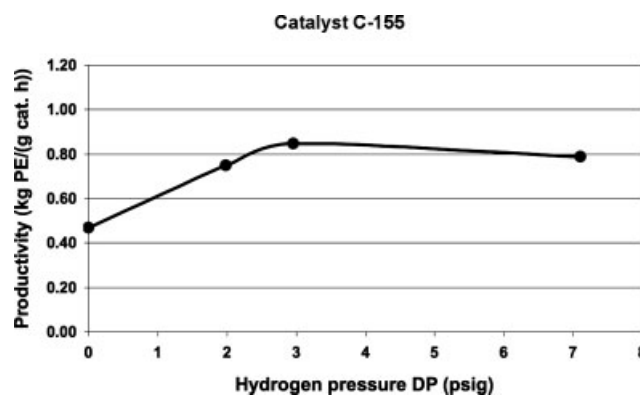
### Measurement of catalyst and resin particle size distribution

The particle size distribution (PSD) of the catalyst and the polymer sample(s) was measured using the computer-interfaced *Mastersizer 2000* particle size analyzer (Malvern Instruments, UK). This instrument works on the principle of laser diffraction. It is equipped with a 50–120 mL capacity Hydro 2000S liquid feeder, which has a built-in ultrasound probe with an online pump and a stirrer.

A small amount of the catalyst sample (about 0.5 g) that shows an obscursion limit of  $\sim 5.0\%$  was dispersed in deionized water. However, for the polymeric sample, a few drops of surfactant were added to water to help dispersion. The optical properties of the samples were selected from the library of materials available in the provided software. Each sample was analyzed using five cycles having various stirrer speeds and different intensities of ultrasound. The PSD and its average were calculated using Mie theory.

### Measurement of catalyst and resin particulate surface morphology

The catalyst and the experimental polyethylene samples were first coated with a layer of carbon to increase the surface conductivity. These coated samples were characterized using a scanning electron



**Figure 2** Effect of hydrogen shock load on the productivity of the experimental catalyst in MAO-free polymerization trials. Polymerization conditions: pressure = 8.5 bar (g); temperature = 75.0°C; time = 1 h.

**TABLE I**  
**Particle Size Distribution (PSD) of the Experimental Catalyst and the Resulting Polyethylenes**

Catalyst and polymer	Hydrogen shock load ( $\Delta P$ , psi)	Volume-weighted mean ( $\mu\text{m}$ )	$d(0.1)$ ( $\mu\text{m}$ )	$d(0.5)$ ( $\mu\text{m}$ )	$d(0.9)$ ( $\mu\text{m}$ )	Span <sup>a</sup>
Experimental catalyst	Does not apply	40.56	12.65	36.83	74.05	1.68
Polyolefins	0.00	235.62	98.07	192.40	369.92	1.41
	1.96	363.66	212.09	348.80	551.31	0.97
	2.96	418.75	243.90	404.21	635.74	0.97
	7.11	451.22	257.00	434.75	693.32	1.00

$d(0.1)$ ,  $d(0.5)$ , and  $d(0.9)$  mean that 10%, 50%, and 90% of the particles have less than or equal to the corresponding indicated particle diameter ( $\mu\text{m}$ ), respectively.

<sup>a</sup> Span =  $[d(0.9) - d(0.1)]/d(0.5)$ .

microscope (SEM) equipped with an energy dispersive X-ray spectrometer. The particulate morphology was evaluated by operating the electron microscope in the backscattered electron imaging mode.

#### Measurement of resin bulk density

The bulk density of the experimental polyethylenes was determined using the Apparent Density Tester (Model No. 1132, manufactured by IPT, Germany) according to ISO 60.<sup>28</sup>

### RESULTS AND DISCUSSION

Hydrogen responsiveness is a characteristic performance indicator for an olefin polymerization catalyst. The present study investigates this aspect for the experimental catalyst using the shock load feeding of hydrogen that refers to the following differential changes in hydrogen pressure:  $\Delta P = 1.96$ , 2.96, and 7.11 psi. These values correspond to feeding the reactor with  $5.47 \times 10^{-4}$ ,  $8.26 \times 10^{-4}$ , and  $19.84 \times 10^{-4}$  mol of hydrogen, respectively. We have calculated the molar masses using the ideal gas law relation. Recall that the experimental catalyst loads 30 wt % MAO (not the 10 wt % analog); and the structure and constituent of MAO vary with its solution concentration. For example, the total aluminum content, aluminum containing free and associated trimethyl aluminum (TMA), aluminum belonging to free and associated TMA relative to total aluminum, and methyl to aluminum ratio of 30 wt % MAO differ from those of the 10 wt % analog.<sup>29</sup>

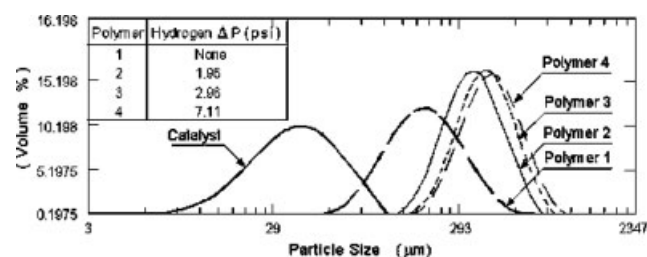
What follows discusses the effects of introducing the aforementioned small amounts of hydrogen on polymerization kinetic profile, catalyst productivity, resin PSD and average particle size, particulate morphology, bulk density, weight average molecular weight, and PDI. The overall findings will be explained in this study by particularly revisiting the ethylene polymerization mechanism, consider-

ing the present shock load mode of hydrogen feeding.

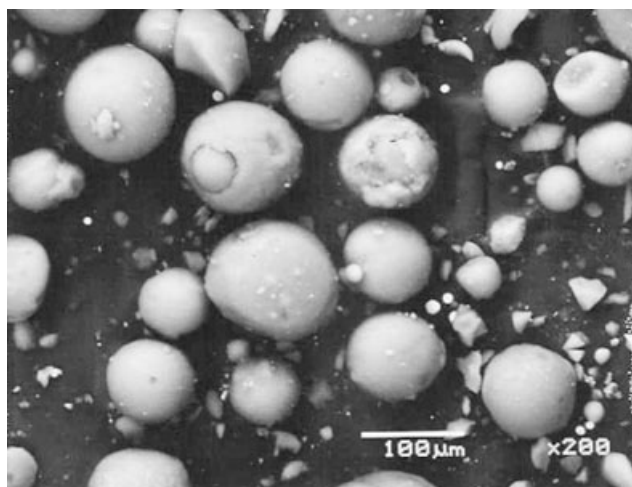
Figure 1 shows the qualitative kinetic profiles of the above catalysts that plot instantaneous ethylene flow rate as a function of the polymerization time. The kinetic profiles are fairly similar and indicate catalytic stability over the polymerization run period. However, each shock load increased the instantaneous flow rate of ethylene over that of the polymerization trial without hydrogen. This finding also showed to be quantitatively reflected in the catalyst productivity, as shown by Figure 2. The catalyst productivity asymptotically increased from  $\sim 0.48$  to 0.85 kgPE/(g cat h) [1.77-fold increment because of hydrogen shock load ] up to a  $\Delta P = \sim 3.0$  psi. Then, it fairly leveled off.

So far as the reactor operability is concerned, no fouling was observed during the experimental MAO-free polymerization trials. Free-flowing polymer particles were obtained with and without hydrogen. Table I and Figure 3 compare the PSD of the catalyst with that of the resulting polyethylenes. Figure 5 show that the PSD of the polymer resembled that of the catalyst. The volume-weighted mean— $d(0.1)$ ,  $d(0.5)$ , and  $d(0.9)$  of the catalyst and the resulting polyethylenes—each showed the following common trend (Table I).

Polyethylene at  $\Delta P = 7.11$  psi > polyethylene at  $\Delta P = 2.96$  psi > polyethylene at  $\Delta P = 1.96$  psi >



**Figure 3** Comparison of the particle size distribution (PSD) of the resulting polyethylenes (with and without shock load of hydrogen) with that of the catalyst.

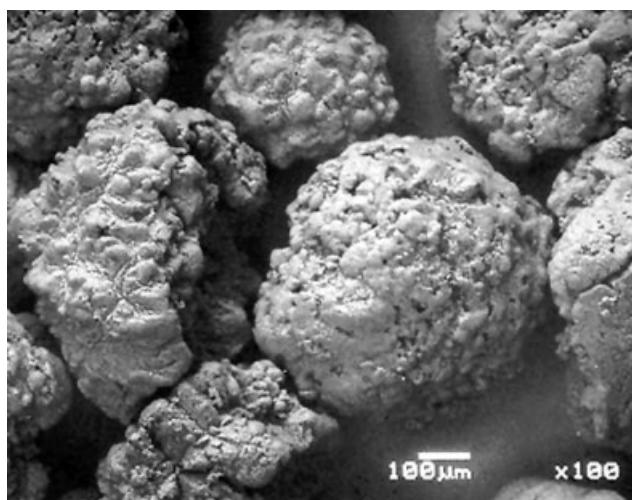


**Figure 4** SEM photograph of the experimental catalyst particles.

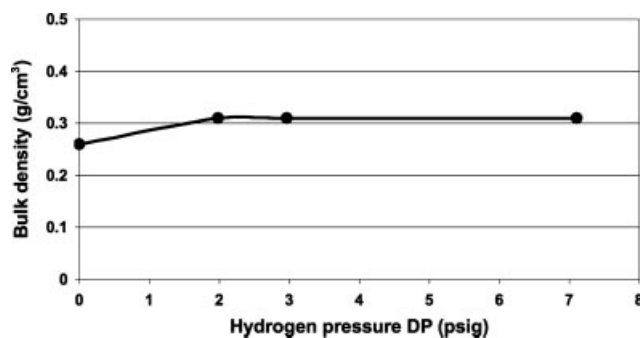
polyethylene without hydrogen shock load > experimental catalyst.

More specifically speaking, the volume-weighted mean particle diameters of the resulting polyethylenes were found to be 5.80, 8.96, 10.32, and 11.12-fold that of the catalyst corresponding to  $\Delta P = 0.00$ , 1.96, 2.96, and 7.11 psi, respectively. Therefore, the hydrogen shock loads facilitated the fragmentation of the catalyst particles during polymerization, and consequently, polymer grew around these fragments increasing the final resin particle size.

Figures 4 and 5—the SEM photographs of the catalyst and the resulting polyethylenes—show that the resin particles are fairly spherical and resemble the catalyst ones.



**Figure 5** SEM photograph of the polyethylene resin particles without hydrogen feeding. MAO cocatalyst-free polymerization trials.



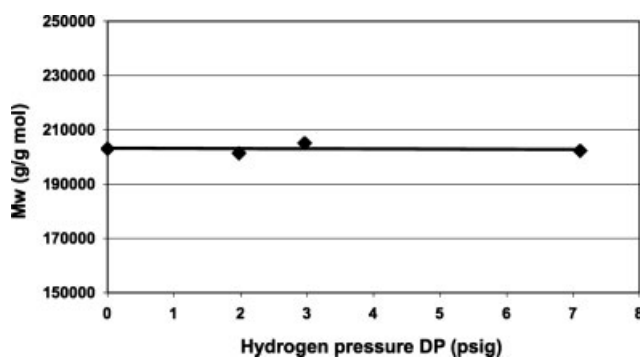
**Figure 6** Effect of hydrogen shock load on the bulk density of the polyethylenes resulting from MAO-free polymerization trials. Polymerization conditions: pressure = 8.5 bar (g); temperature = 75.0°C; time = 1 h.

All the earlier findings (Table I, Figs. 3–5) confirm the occurrence of the replication phenomenon from the catalyst to the polymer.

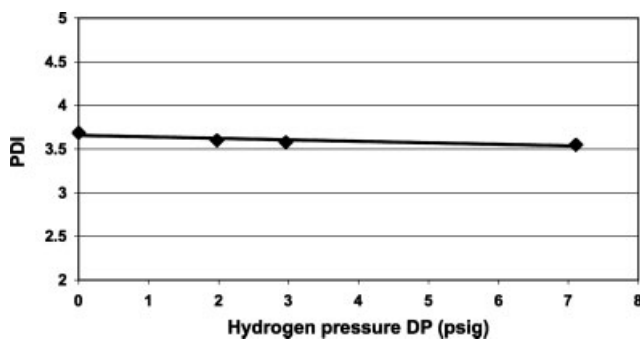
Another spectacular finding, with respect to hydrogen shock load, was noticed with the bulk density. The bulk density qualitatively varied as the catalyst productivity did (see Fig. 6). It increased from 0.26 to 0.31 g/cm<sup>3</sup> up to a  $\Delta P = \sim 3.0$  psi. This finding is an eventual consequence of catalyst fragmentation, subsequent polymer particle growth, and increase in catalyst productivity.

Figures 7 and 8 respectively, show that neither  $M_w$  nor PDI of the resulting polyethylenes practically differed as a function of hydrogen shock load dosages. What follows now explains the earlier overall findings.

In absence of hydrogen, (See Scheme 1) the growing polymer chains get terminated through  $\beta$ -hydride elimination which, in parallel, forms a metal-hydride ( $Zr^+-H$ ) compound on the catalyst surface. However, because of strong  $\beta$ -agostic interaction between the H atoms of the incoming ( $C_2H_4$ ) molecules and the Zr atom, the  $Zr^+-H$  bond is rela-



**Figure 7** Effect of hydrogen shock load on the weight average molecular weight of the polyethylenes resulting from MAO-free polymerization trials. Polymerization conditions: pressure = 8.5 bar (g); temperature = 75.0°C; time = 1 h.



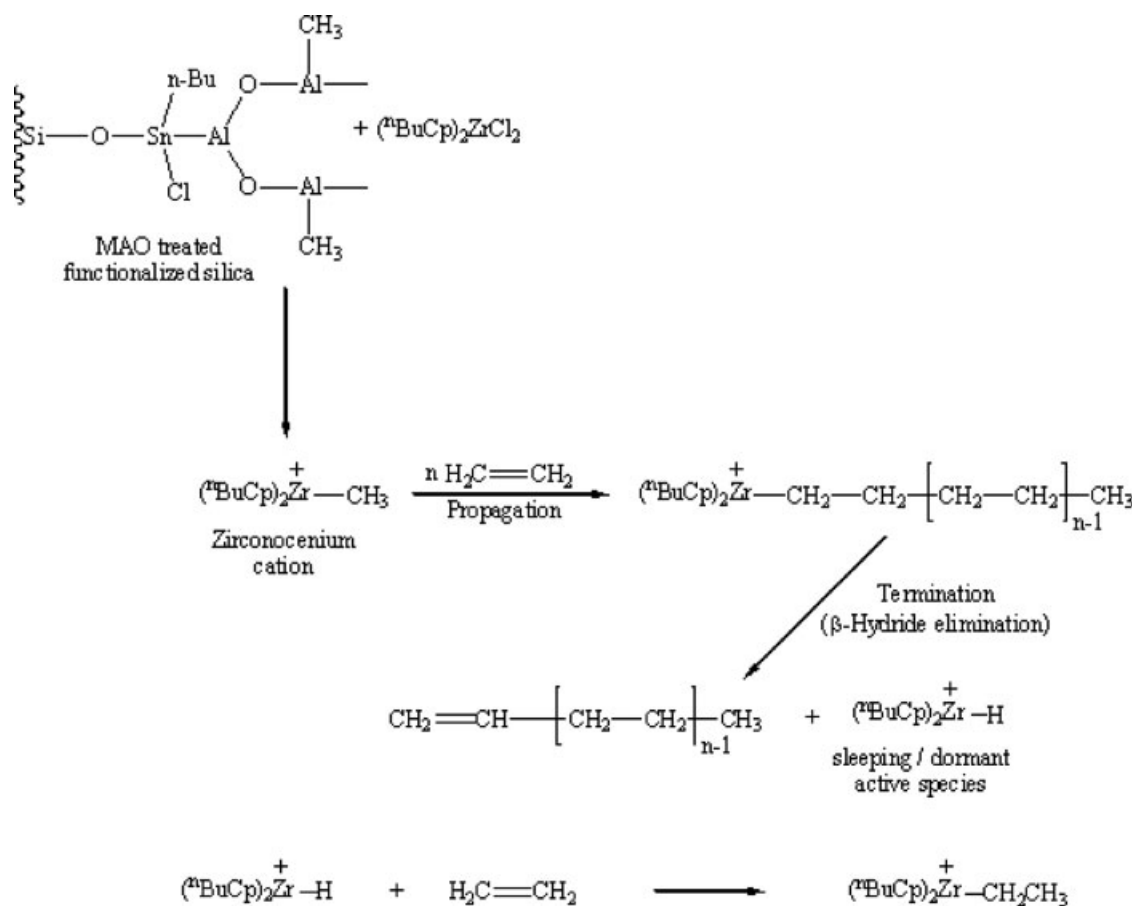
**Figure 8** Effect of hydrogen shock load on the polydispersity index (PDI) of the polyethylenes resulting from MAO-free polymerization trials. Polymerization conditions: pressure = 8.5 bar (g); temperature = 75.0°C; time = 1 h.

tively stable. Hence, the  $Zr^+-H$  bond does not insert ethylene. It remains as a dormant/sleeping catalytic species.<sup>30</sup> Now we review the work of Zakharov et al.,<sup>31</sup> who conducted an FTIR spectroscopic study of ethylene polymerization catalyzed by silica-supported Group IV B organometallic compounds. They confirmed the following. The metal-

hydride compound formed on the silica surface, in the presence of hydrogen, inserted ethylene; and the catalytic activity increased with the increase in the number of catalytic active sites. Therefore, hydrogen, depending on polymerization conditions, can overcome the afore-said  $\beta$ -agostic interaction, showing rate-enhancement effect.

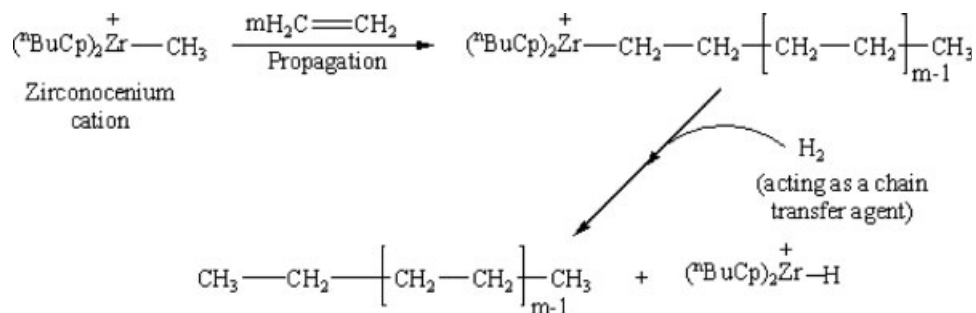
The earlier arguments suit to explain the findings of the present MAO cocatalyst-free ethylene polymerization study. That the ethylene consumption rate and the catalyst productivity of the experimental catalyst increased in the absence of MAO cocatalyst may, therefore, be attributed to (a) activating the dormant/sleeping catalytic species  $Zr^+-H$  by the hydrogen shock load (Scheme 1) and (b) the absence of competitive diffusion between ethylene and the separately fed MAO. For such findings to take place, we observe that both these factors as well as a limiting concentration of hydrogen (which does not enhance chain transfer and termination processes) are necessary.

The works of Chu et al.<sup>8,9</sup> also support the requirement of the absence of competitive diffusion between ethylene and the separately fed MAO. They



**Scheme 1** Mechanism of ethylene polymerization without hydrogen. This shows to apply to the MAO cocatalyst-free ethylene polymerization with shock load feeding of hydrogen.





**Scheme 2** Mechanism of ethylene polymerization with hydrogen working as a chain transfer agent.

studied the effect of hydrogen on ethylene polymerization using *in situ* supported  $\text{Cp}_2\text{ZrCl}_2$  and  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ . Here, these metallocenes contacted MAO-loaded silica during polymerization at an Al:Zr molar ratio of 500; MAO was not used as an external cocatalyst. Hence, no competitive diffusion between ethylene and MAO occurred. The rate enhancement effect due to hydrogen also prevailed in these studies. However, the peak molecular weight dropped with the increase in hydrogen pressure.

The present findings differ from those of ethylene polymerization (under comparable hydrogen shock load and polymerization conditions) caused by the catalyst, silica/10 wt % MAO/ $\text{Cp}_2\text{ZrCl}_2$ , in the presence of the separately fed MAO-cocatalyst at an Al:Zr molar ratio of 1000. Here, the catalyst activity and  $M_w$  decreased with the increasing hydrogen shock load.<sup>32</sup> Therefore, in this MAO-cocatalyzed situation,<sup>32</sup> the hydrogen shock load reduced the rate of chain growth, acted as a strong chain transfer agent, and increased the rate of chain termination reaction. See Scheme 2.

## CONCLUSIONS

The present MAO cocatalyst-free slurry ethylene polymerization, catalyzed by the supported catalyst  $\text{SiO}_2$ - $n\text{BuSnCl}_3$ /MAO/ $(n\text{BuCp})_2\text{ZrCl}_2$ , concludes the following:

- i. The catalyst showed fairly stable polymerization kinetics.
- ii. The shock load feeding of hydrogen increased the ethylene consumption (at a fairly constant rate), catalyst productivity, as well as the resin bulk density and average particle size at  $\Delta P$  (of hydrogen)  $\geq \sim 3.0$  psi. This shows a procedure for overcoming the inherent drop in catalyst productivity caused by heterogenization of metallocenes (that is a method for catalyst activation) and improving the resulting resin bulk density.

- iii. The bulk density increased from 0.25 to 0.31  $\text{g}/\text{cm}^3$ .
- iv. The volume-weighted mean particle diameter of the resulting polyethylenes was found to be 5.80–11.12-fold that of the catalyst corresponding to  $\Delta P = 0.00$ –7.11 psi, respectively.
- v. The span of PSD of the polyethylenes resulting from shock load of hydrogen showed to be approximately one<sup>1</sup> and less than that of the polyethylene obtained without hydrogen (1.41).
- vi. No reactor fouling was observed. Free-flowing polymer particles with a spherical morphology similar to that of the catalyst particles were obtained. The PSD of the resulting polyethylenes resembled that of the catalyst. Therefore, the *replication phenomenon* from catalyst to polymer took place.
- vii. The shock load hydrogen feeding did not affect  $M_w$  and PDI of the synthesized polyethylenes.
- viii. On the basis of the above findings, the mechanism of ethylene polymerization under the present experimental conditions has been revisited. A revised polymerization mechanism has been postulated.

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