

## **A comparison of $\text{Cp}_2\text{HfCl}_2$ versus $\text{Cp}_2\text{ZrCl}_2$ methylalumoxane catalysts**

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### Summary

Ethylene polymerizations by  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  (MAO = methylalumoxane) and  $\text{Cp}_2\text{HfCl}_2/\text{MAO}$  catalysts are compared. The Hf catalysts have about two-thirds the activity of the Zr catalysts. This difference may be attributed to the greater number of active centers present in the Zr catalyst. The Hf catalyst shows a smaller dependence of: (1) polymer MW on temperature and (2) polymerization activity on transition metal concentration than the Zr catalyst.

### Introduction

Titanocene dichloride ( $\text{Cp}_2\text{TiCl}_2$ ) when activated by organoaluminum halides was first shown by Breslow and Newburg to function as a homogeneous olefin polymerization catalyst (1). A bimetallic complex having tetravalent titanium was found to be the active species. The catalyst suffered from rapid deactivation by bimolecular reductive disproportionation (2). The inactive trivalent titanium species could be reactivated by oxidation with oxygen. Sinn, Kaminsky and coworkers subsequently investigated zirconocene dichloride ( $\text{Cp}_2\text{ZrCl}_2$ ) for ethylene polymerization (3,4). These titanium and zirconium catalyst systems exhibit only modest productivity of polyethylene, produce polymer of relatively low molecular weight, and do not polymerize higher olefins.

A major advance in the application of group 4 metallocene-type catalysts for Ziegler-Natta polymerizations occurred when Kaminsky and coworkers discovered that a combination of either  $\text{Cp}_2\text{MCl}_2$  (M=Ti,Zr) or halide-free  $\text{Cp}_2\text{M}(\text{CH}_3)_2$  systems and oligomeric methylalumoxanes (MAO) (formed from  $(\text{CH}_3)_3\text{Al}$  and a source of  $\text{H}_2\text{O}$ ) were exceedingly active catalysts, and rapidly polymerized propylene as well as ethylene (4-6). Ewen independently showed that the soluble catalyst system  $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)_2/\text{MAO}$  produced isotactic polypropylene with a novel stereoblock microstructure (7). Moreover, chiral catalysts derived from racemic ethylenebis(indenyl)- and ethylenebis-(tetrahydroindenyl)-titanium or -zirconium dichlorides were found to be capable of the stereospecific polymerization of propylene (7,8).

In spite of these rapid developments in the field of homogeneous Ziegler-Natta polymerization catalysts, virtually nothing has been reported concerning the relative catalytic activity of corresponding organohafnium systems. Kaminsky et al. have stated qualitatively that for ethylene polymerizations employing  $\text{Cp}_2\text{M}(\text{CH}_3)_2/\text{MAO}$  (M = Ti, Zr, Hf), the zirconium catalyst

is more active than the titanium or hafnium systems, especially at temperatures over 50°C (9). The most definitive comparison has very recently been made by Ewen et al., who examined the catalytic properties of racemic ethylenebis(indenyl)-hafnium dichloride and racemic ethylene bis(tetrahydroindenyl)hafnium dichloride versus their zirconium analogs as propylene polymerization catalysts (10). While the two metals exhibited similar catalyst activities, the hafnium systems produced much higher molecular weight isotactic polypropylene, and the hafnium-produced polymers were slightly more stereoregular than those obtained with analogous zirconium catalysts.

In view of the general lack of information on hafnium-based olefin polymerization catalysts, we have undertaken a program of research designed to evaluate such systems. In this paper, we report on the use of  $\text{Cp}_2\text{HfCl}_2/\text{MAO}$  as an ethylene polymerization catalyst, and compare its properties with the better-known zirconium analog.

### Experimental

$\text{Cp}_2\text{HfCl}_2$  was synthesized according to the method of Rausch et al. (11), using 99.99% pure  $\text{HfCl}_4$  on a metal-metal basis (Research Organic/Inorganic Chemicals Co.) Procedures for the preparation of MAO (12), polymerization of ethylene (13), determination of total metal-polymer bond concentration (14), measurement of viscosity and calculation of viscometric molecular weight (13), are as previously given.

### Results and Discussion

Typical polymerization profiles are shown in Figure 1. For the  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  system the maximum rate of polymerization,  $R_{p,m}$  was reached immediately upon the addition of the catalyst.

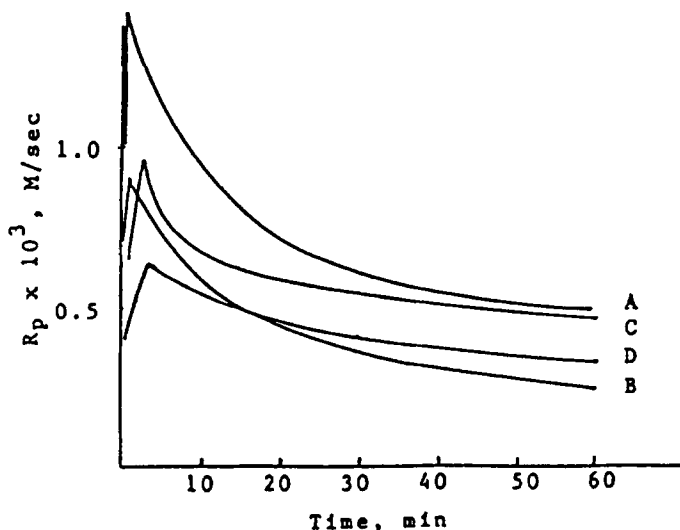


Figure 1. Ethylene polymerization profiles for  $\text{Cp}_2\text{ZrCl}_2$  (A) 70°C; (B) 50°C; for  $\text{Cp}_2\text{HfCl}_2$  (C) 70°C; (D) 50°C. Other polymerization conditions:  $[\text{TM}] = 48 \mu\text{M}$ ,  $[\text{Al}] = 56 \text{ mM}$ ,  $P(\text{C}_2\text{H}_4) = 1.7 \text{ atm}$ .

In contrast, there was a rate build up during the first few minutes of ethylene polymerization for the Hf catalyst. At a given transition metal and MAO concentration and temperature, the Hf catalyst had a maximum rate of polymerization,  $R_{p,m}^-$ , which is about two-thirds that of the Zr catalyst. On the other hand, there is about a three-fold rate decay for the Zr catalyst but a smaller two-fold rate decay for the Hf catalyst.

The initial number of active sites,  $[C^*]_0$ , was counted using a radiolabeling technique. Polymerization was quenched with tritiated methanol; from the plot of specific activity versus yield  $[C^*]_0$  was obtained by extrapolation as shown in Figure 2. The intercept gives  $[C^*]_0$  to be 52% of the  $Cp_2HfCl_2$ . Previously the  $[C^*]_0$  for the  $Cp_2ZrCl_2/MAO$  catalyst was determined under the same conditions of Figure 2, and was found to be 80%. Thus, the ratio of the  $[C^*]_0$  (Hf)/ $[C^*]_0$  (Zr) = 0.65 which agrees with the ratio of  $R_{p,m}^-$  for the two catalysts. Therefore, the rate constants for propagation are nearly the same for the Hf and Zr catalysts.

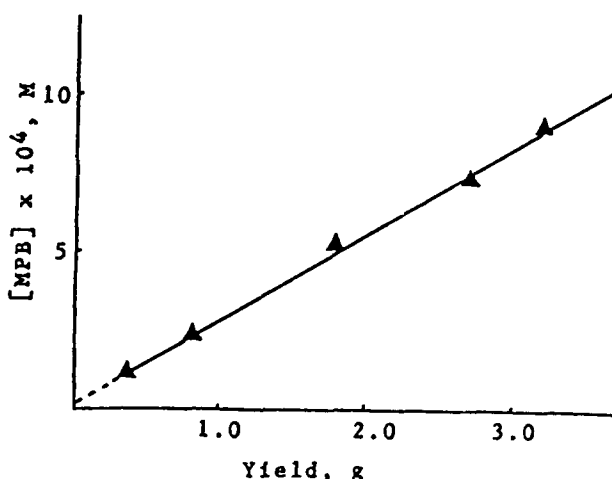


Figure 2. Variation of metal-polymer-bond concentration with polymerization yield:  $[Cp_2HfCl_2] = 48 \mu M$ ;  $[MAO] = 56 mM$ ; temp. =  $70^\circ C$ .

The two catalysts were compared under various polymerization conditions; the results are summarized in Table 1 and Figures 3 & 4. At a modest ratio of MAO to transition metal,  $Al/TM = 1.17 \times 10^3$ , the two catalysts show the same temperature dependence for activity of only 2.5 kcal mol<sup>-1</sup>. The overall activation energy for the polymerization is smaller than diffusion activation energy. The Zr catalyst has a large sensitivity of MW on temperature, since  $M_v$  decreases 20-fold between  $25^\circ C$  and  $70^\circ C$ ; the decrease is only 5-fold with the Hf catalyst. The polymer obtained with the Hf catalyst at  $70^\circ C$  has a higher MW than the Zr catalyst. The converse is true for  $25^\circ C$  polymerizations.

Table I. Polymerization activities for  $\text{Cp}_2\text{HfCl}_2$  and  $\text{Cp}_2\text{ZrCl}_2$  - MAO catalysts.<sup>a</sup>

Metalocene	Conc. ( $\mu\text{M}$ )	Temp, $^\circ\text{C}$	Activity <sup>b</sup> $\times 10^{-6}$	$\overline{M}_v \times 10^{-5}$
Zr	48	25	0.45	2.0
Zr	48	50	0.89	0.65
Zr	48	70	1.3	0.11
Hf	48	25	0.29	0.98
Hf	48	50	0.56	0.67
Hf	48	70	0.88	0.20
Zr	4.8	25	3.9	2.5
Zr	4.8	50	7.0	0.82
Zr	4.8	70	14	0.27
Hf	4.8	25	0.53	1.3
Hf	4.8	50	1.2	1.1
Hf	4.8	70	3.8	0.45

<sup>a</sup> [MAO] = 56 mM,  $P(\text{C}_2\text{H}_4) = 1.7$  atm.

<sup>b</sup> (gm of polyethylene)/(mole of catalyst)(atm. of  $\text{C}_2\text{H}_4$ )(hr.)

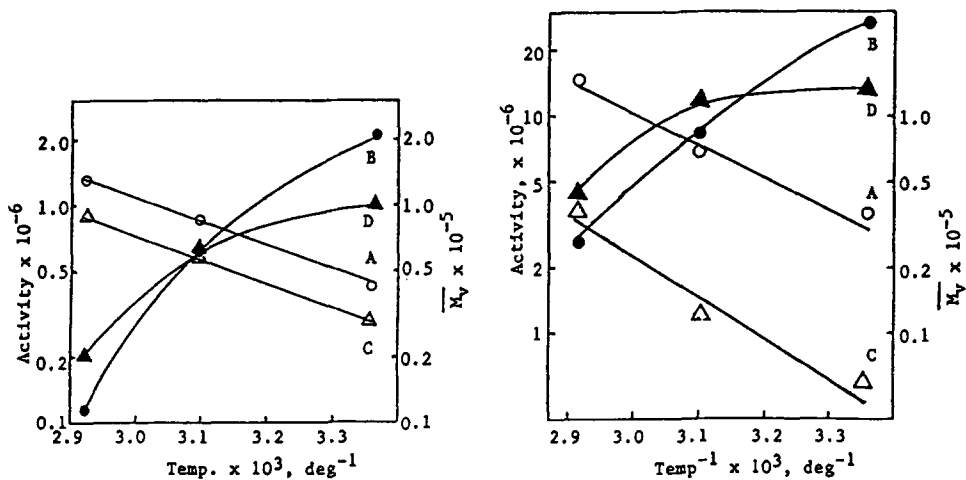


Figure 3 (left). Comparison of the  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  catalyst: (A) activity and (B)  $\overline{M}_v$  versus  $1/\text{temp}$  with the  $\text{Cp}_2\text{HfCl}_2/\text{MAO}$  catalyst: (C) activity and (D)  $\overline{M}_v$  versus  $1/\text{temp}$  at  $[\text{TM}] = 48 \mu\text{M}$ ,  $[\text{Al}] = 56 \text{ mM}$ ,  $P(\text{C}_2\text{H}_4) = 1.7$  atm.

Figure 4 (right). Comparison of the  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  with the  $\text{Cp}_2\text{HfCl}_2/\text{MAO}$  catalyst at  $4.8 \mu\text{M}$  conc. and  $\text{Al}/\text{TM} = 1.17 \times 10^4$ . Symbols are the same as in Figure 3.

The activity of the  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  catalyst has been found to be inversely proportional to the Zr concentration (15,16). This was interpreted as a decrease of bimolecular deactivation. In contrast, the variation of activity with Hf concentration is less pronounced (Table 1). At the low [TM] and high [Al]/[TM] =  $1.17 \times 10^4$ , the activity is more temperature dependent than at the lower [Al]/[TM] ratio.

The results of this study help show the complexity of metallocene/MAO catalysts. Depending upon the polymerization conditions of [TM], [MAO], and temperature, the polymer obtained with the Hf catalyst can have higher MW ( $>50^\circ\text{C}$ ) or lower MW ( $<50^\circ\text{C}$ ) than with the Zr catalyst. There is greater utilization of the transition metal in the Zr catalyst than the Hf catalyst.

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