

## SHORT COMMUNICATIONS

# The Catalytic Activity of Bis-cyclopentadienyltransitionmetal Compounds for Ethylene Polymerization

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The catalytic activity of the binary system of the biscyclopentadienyltransitionmetal compound and of the organoaluminum compound has been investigated. The transition metal  $\pi$ -complexes used as components of the binary system were biscyclopentadienyltransitionmetal halide, -chromate, -dichromate, -phosphate, -thiocyanate, -tetrathiocyanatodiamminechromate (VI), etc., while the center elements of the  $\pi$ -complexes tried were titanium, vanadium and zirconium.

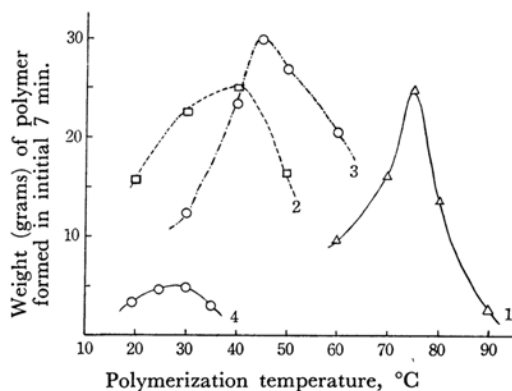


Fig. 1. Catalytic activity of the binary system for ethylene polymerization at various temperature.

1.  $\text{Cp}_2\text{TiCr}_2\text{O}_7 - \text{AlEt}_2\text{Cl}$
2.  $\text{Cp}_2\text{TiCr}_2\text{O}_4 - \text{AlEt}_2\text{Cl}$
3.  $\text{Cp}_2\text{Ti}[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2 - \text{AlEt}_2\text{Cl}$
4.  $\text{Cp}_2\text{Ti}[(\text{NH}_3)_2\text{Cr}(\text{SCN})_4]_2 - \text{AlEt}_2\text{Cl}$

Figure 1 shows the relations of the polymerization temperature and the weight of the polymer formed during the initial seven minutes by the binary catalyst systems of 0.1 g. of biscyclopentadienyltitanium compounds and 1 cc. of  $\text{AlEt}_2\text{Cl}$ , using 50 cc. of toluene as a solvent under 40 kg./ $\text{cm}^2$  of ethylene pressure. The temperature at which the catalyst system showed a maximum activity was 75°C in the  $\text{Cp}_2\text{TiCr}_2\text{O}_7 - \text{AlEt}_2\text{Cl}$  system, 50°C in the  $\text{Cp}_2\text{TiCr}_2\text{O}_4 - \text{AlEt}_2\text{Cl}$  system, and 45°C in the  $\text{Cp}_2\text{Ti}[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2 - \text{AlEt}_2\text{Cl}$  system.

When vanadium or zirconium was the center element instead of titanium, the same tendency was observed.

The results are summarized in Table I and Table II. In Table I the temperature of the maximum

TABLE I. THE TEMPERATURE (°C) OF THE MAXIMUM CATALYTIC ACTIVITY OF THE  $(\text{Cp}_2\text{MX}_2 - \text{AlEt}_2\text{Cl})$  SYSTEM

M: Ti, V, Zr.			
Center element	Ti	V	Zr
Anion species			
$\text{Cl}^- (\text{Br}^-)^*$	25	25	30
$\text{Cr}_2\text{O}_7^{2-}$	75	75	80
$\text{CrO}_4^{2-}$	40	40	50
$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}^-$	45	45	50
$[(\text{NH}_3)_2\text{Cr}(\text{SCN})_4]^-$	30	30	40
$\text{PO}_4^{3-}$	30	30	40

\*  $\text{Cp}_2\text{ZrBr}_2$

catalytic activity of the system is shown for each center element of titanium, vanadium, zirconium. In Table II the maximum catalytic activity of each binary system (the transitional  $\pi$ -complex- $\text{AlEt}_2\text{Cl}$ ) is shown. The catalytic activity is expressed as grams of polymer formed in an hour per gram of transition metal complex under the experimental conditions.

TABLE II. THE MAXIMUM CATALYTIC ACTIVITY OF THE SYSTEM

Center element	Ti	V	Zr
Anion species			
$\text{Cl}^- (\text{Br}^-)^*$	31740	130	15
$\text{Cr}_2\text{O}_7^{2-}$	2180	100	2.2
$\text{CrO}_4^{2-}$	2100	75	4.4
$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}^-$	2580	8200	2.4
$(\text{NH}_3)_2\text{Cr}(\text{SCN})_4^-$	330	50	7.2
$\text{PO}_4^{3-}$	40	20	0.9

\*  $\text{Cp}_2\text{ZrBr}_2$

Therefore, the following points were concluded.

1) The activity of the catalyst system depends principally on the nature of the center element of the  $\pi$ -complex, and the order of catalytic activity is conspicuous;



2) The temperature of the maximum catalytic activity of the binary system depends on the anion species of the  $\pi$ -complex, and it is independent of the center element.

3) Exceptionally, the system of biscyclopentadienylvanadiumpicric acid  $\approx$  aluminumdiethylchloride is extraordinarily active at 45°C.

4) As an organoaluminum compound,  $\text{AlEt}_2\text{Cl}$  is better than  $\text{AlEt}_3$ ,  $\text{AlEtCl}_2$ ,  $\text{Al}(\text{i-Bu})_3$ , etc.