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STUDIES ON HOMOGENEOUS Cp_2MCl_2-$Et_3Al + R_3SiCl$ CATALYST SYSTEM FOR ETHYLENE POLYMERIZATION

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ABSTRACT

Homogeneous catalyst system, $Cp_2MCl_2/Et_3Al + R_3SiCl$ ($Cp = \eta^5 = C_5H_5$; M = Ti, Zr; R=Me, Ph), polymerizes ethylene in toluene medium. The activity of such catalyst systems are governed by the factors like nature of metallocene dichloride, chlorosilane, and polymerization parameters such as Al/M, Si/Al molar ratios and temperature. It is observed that zirconocene dichloride system shows higher polymerization efficiency as compared to titanium analogues. Furthermore, the use of trimethylchlorosilane in combination with triethylaluminum (TEAL) as cocatalyst yields more polymer in comparison to triphenylchlorosilane and TEAL system.

INTRODUCTION

Heterogeneous Ziegler-Natta catalyst systems have been extensively investigated for the olefin polymerization [1-3]. This has provided a foundation to evolve high performing commercial catalyst for the production of polyolefins. In recent past, however, metallocene based catalysts have attracted considerable

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attention [4,5] due to their unique capability of producing the polymers of defined structure. It also offers possibility of polymerizing a wide range of olefines including functional ones. Metallocene systems comprising of Cp_2TiCl_2/R_2AlCl was the first homogeneous combination found to be active for ethylene polymerization [6-9]. The use of aluminoxanes as cocatalyst has significantly improved the performance of metallocene for ethylene polymerization [10-14]. Further enhancement in the efficiency was achieved by modifying the structure of metallocenes and aluminoxanes [4,15]. The polymerization parameters also played a regulatory role in optimizing the productivity and controlling the properties of polymers.However, the limitations with aluminoxanes interms of requirement of larger quantities and ambiguous chemical composition have led researcher to look for metallocene systems which can either perform with lesser amount of aluminoxanes or without it.The present study examines the performance of metallocenes in combination with modified alkylaluminum as cocatalyst for ethylene polymerization . The trialkyl aluminium has ability to form adduct with -Cl , -OH, and -OR bonded compounds [16].Such adducts can undergo ligand rearrangement leading to modification of alkylaluminum . The modified aluminium compound would, therefore, be expected to provide finer control over reducing behaviour and alkylating nature of alkylaluminum.

EXPERIMENTAL

Materials : Bis(cyclopentadienyl)titanium dichloride, Bis(cyclopentadienyl)zirconium dichloride, triethylaluminum, trimethylchlorosilane, and triphenylchlorosilane were used as received. Toluene was used after drying over sodium wire. Ethylene (polymerization grade) was obtained from the commercial plant and used as such.

All experimental manipulations were carried out under ultra high pure nitrogen atmosphere using Vacuum Atmosphere Model HE-43-2 Dri Lab equipped with a model HE 491 Dri Train and Schlenk techniques.

Ethylene Polymerization : Polymerization of ethylene was carried out in a 500 ml glass reactor equipped with a magnetic stirrer. Calculated amount of cocatalyst and R_3SiCl (R=Me,Ph) were mixed in 20 ml toluene. This solution was added into 180 ml toluene containing metallocene dichloride. Ethylene was continuously supplied to the reactor at selected temperature and 1 bar pressure. The polymerization was carried for a fixed period of time and at the end methanolic hydrochloride was added to terminate the polymerization . The polymer thus obtained was dried in vacuo.

RESULTS AND DISCUSSION

The performance of titanocene dichloride in conjunction with TEAL as cocatalyst was examined for the ethylene polymerization. Polymer formation was not observerd even after 2 hrs of the reaction. However, zirconocene dichloride along with TEAL gave polyethylene (45 g PE/mmol Zr). These results [8,9,17,18] indicate that metallocene dichloride reacts with TEAL to generate an alkylated species(Eq.1) The alkylated compound undergo coordination and propagation reactions with ethylene to give polyethylene(Eq.2). The active species on reduction generates an inactive complex(Eq.3). The higher resistance of alkylated zir-

$$Cp_2MCl_2 + 1/2\ (Et_3Al)_2 \longrightarrow Cp_2MCl(Et)\cdot Et_2AlCl \quad (1)$$

$$Cp_2MCl(Et)\cdot Et_2AlCl + nC_2H_4 \longrightarrow Cp_2MCl(C_2H_4)_nEt\cdot Et_2AlCl \quad (2)$$

$$2Cp_2\ MCl(Et)\cdot Et_2AlCl \longrightarrow Et_2AlCl\cdot Cp_2MCl(CH_2)_2\ MClCp_2\cdot Et_2AlCl + C_2H_6 \longrightarrow Cp_2M(III)\ Complex + CH_2 = CH_2 \quad (3)$$

nium compound towards reduction as compared to titanium analogue may be the reason for polymer formation in zirconocene system.

The transformation of active metallocene into inactive species can be controlled by retarding the reducing capability of trialkylaluminum. Thus, TEAL was mixed with chlorosilane before reacting with metallocene dichloride. TEAL reacts with the R_3SiCl to generate Al, Si adduct which may undergo ligand exchange reaction to give chloroalkylaluminum compound.

The polymerization of ethylene was carried out with $Cp_2MCl_2.Et_3Al + Me_3SiCl$ catalyst system. The results (Table 1) show that metallocene in combination with TEAL and trimethylchlorosilane as cocatalyst shows activity for ethylene polymerization. Zirconocene system was, however, relatively more productive than the titanocene . Effect of polymerization parameters on productivity was studied to optimize effeciency of catalyst systems.

Effect of Temperature

The activity of $Cp_2TiCl_2/Et_3Al + Me_3SiCl$ was investigated at different temperatures. The results indicate (Figure 1) that the increase of temperature from 10 to 25°C leads to increase in activity by approximately two fold. Further rise in temperature lowers the productivity. Comparison of the results between titanocene and zirconocene indicate that zirconocene system shows optimum performance at 40°C whereas titanium system performs optimally at 25°C. It may be due to better stability of the active zirconium complex at relatively higher temperature.

Effect of Al/M molar ratio

The effect of Al/M molar ratio on the activity of $Cp_2MCl_2/Et_3Al + Me_3SiCl$ (M=Ti,Zr) was examined. The data (Figure 2) indicate that the increase of Al/Ti ratio in Cp_2TiCl_2 system

Table - 1 **Performance of metallocene dichloride systems for ethylene polymerization**

Catalyst System	Polymer yield[a]
Cp_2TiCl_2/Et_3Al	nil
$Cp_2TiCl_2/Et_3Al+Me_3SiCl$	157
Cp_2ZrCl_2/Et_3Al	45
$Cp_2ZrCl_2/Et_3Al+Me_3SiCl$	260

[a] Polymerization conditions : P_{C_2}=1 atm, toluene 200 ml, metallocene dichloride = 100 mg, Al/M molar ratio = 15, Si/Al molar ratio=1.5, temperature 25°C. Time = 2h. M=Ti, Zr, Polymer Yield in g PE/mmol M.

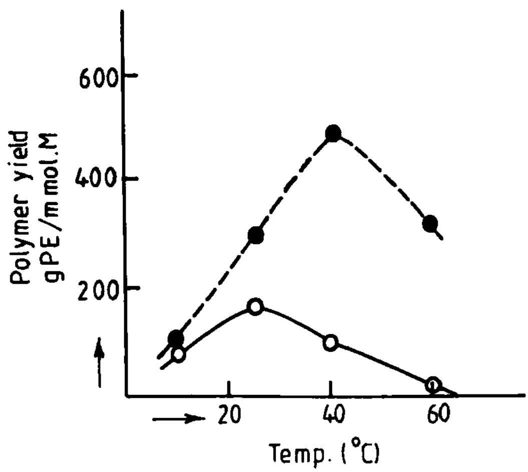

Figure -1. Effect of temperature on polymer yield; (●) Cp_2ZrCl_2/Et_3Al + Me_3SiCl system, Al/Zr=25; (O) Cp_2TiCl_2/Et_3Al + Me_3SiCl system, Al/Ti=15; Other conditions similar to listed in Table 1.

from 5 to 15 incr ases polymer yield by 32%. Further increase in the ratio from 15 to 100 reduces polymer formation. In contrast to titanium system, $Cp_2ZrCl_2/Et_3Al + Me_3SiCl$ catalyst (Figure 2) gave more polymer with the increase in Al/Zr ratio from 5 to 25. Further increase in the ratio reduces the polymer yield. Comparison of these systems revealed that productivity of zirconium system is more at higher Al/M ratio as compared to analogous titanium system.

Effect of Si/Al Molar Ratio

The concentration of Me_3SiCl was varied to study the effect of Si/Al ratio on the performance of metallocene dichloride system. The data (Figure 3) indicate that both metallocenes show higher formation of polymer upto Si/Al ratio of 1.5. Further increase in the ratio viz. 2.0 reduces the polymer yield. A 42% decrease in the polymer yield is noted in titanium system while zirconium system shows only 18% reduction in the productivity. The data indicate that Si/Al ratio < 1.5 has activating effects in both titanium and zirconium system while higher Si/Al ratio >1.5 retards the polymer formation.

Effect of the nature of chlorosilane and aging time

Effect of various chlorosilanes on the performance of zirconocene dichloride system was examined. The results indicate (Table 2) that the trimethylchlorosilane system shows higher activity than triphenylchlorosilane under similar Si/Al molar ratio. The polymer yield varies in both the silane systems with the variation in Si/Al ratios. In case of trimethylchlorosilane, polymer yield increases with the increase of Si/Al ratio from 0.5 to .5. Further increase in the ratio leads to decrease in the polymer yield. On the other hand, triphenylchlorosilane showed 30% ncrease in the polymer yield with the change of molar ratio

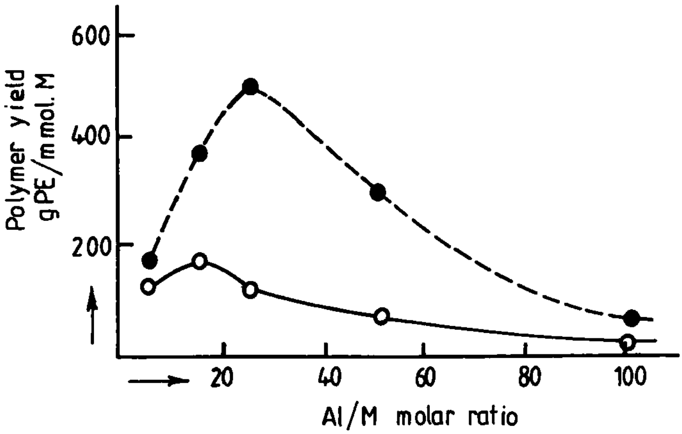

Figure-2. Effect of Al/M molar ratios on Polymer yield; (●) Cp_2ZrCl_2/Et_3Al + Me_3SiCl system, Temp. 40°C; (O) Cp_2TiCl_2/Et_3Al + Me_3SiCl system, Temp. 25°C; other conditions similar to listed in Table - 1.

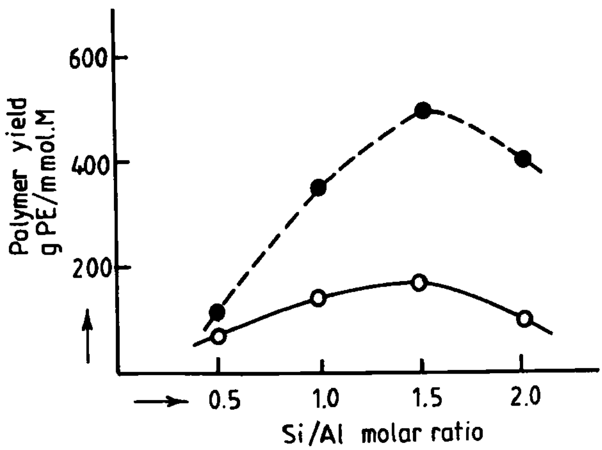

Figure-3. Effect of Si/Al molar ratios on polymer yield; (●) Cp_2ZrCl_2/Et_3Al + Me_3SiCl system, Temp. 40°C, Al/Zr=25; (O) Cp_2TiCl_2/Et_3Al + Me_3SiCl system, Temp. 25°C, Al/Ti=15; other conditions similar to listed in Table-1.

Table - 2 Influence of the nature of triorganochlorosilane in ethylene polymerization with $Cp_2ZrCl_2/Et_3Al + R_3SiCl$ system[a].

Si/Al molar ratio	Me_3SiCl Polymer Yield	Ph_3SiCl Polymer Yield
0.5	109	72
1.0	354	264
1.5	500	345
2.0	401	370

[a] Polymerization conditions : Pc_2=1 atm, toluene 200 ml, Cp_2ZrCl_2 = 100 mg, Al/M molar ratio = 25, temperature 40°C, Time 2h, Polymer yield in g PE/mmol Zr.

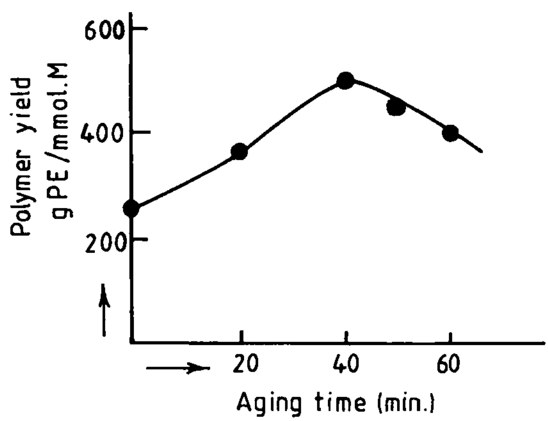

Figure-4. Effect of aging time between Et_3Al and Me_3SiCl on polymer yield; catalyst system $Cp_2ZrCl_2/Et_3Al + Me_3SiCl$, Al/Zr=25, Temp. 40°C, other conditions similar to listed in Table-1.

from 1.0 to 1.5 while further increase in the ratio from 1.5 to 2.0 lead to only 7% increase.

The effect of aging time between the reaction of TEAL and trimethylchlorosilane on the efficiency of zirconocene dichloride was investigated. The results indicate (Figure 4) that the productivity of the catalyst system improves by approximately two fold with the increase of aging time upto 40 minutes. Further increase in the time lowers the polymer yield.

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