

High Activity Mixed Metal Alkyl Cocatalysts for α -Olefin Polymerization*

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Synopsis

High activity α -olefin polymerization catalysts are generally obtained by mixing MgCl_2 -supported TiCl_4 ($\text{MgCl}_2/\text{TiCl}_4$) with an aluminum trialkyl cocatalyst. Surprisingly, AlEt_2Cl , which is the preferred cocatalyst in polymerizations employing nonsupported Ti compounds, is a poor cocatalyst when used with $\text{MgCl}_2/\text{TiCl}_4$. It was found that in propylene and 1-butene polymerizations, using different $\text{MgCl}_2/\text{TiCl}_4$ catalysts, the cocatalyst activity of AlEt_2Cl can be greatly improved by the addition of a magnesium or lithium alkyl. The mixed metal alkyl obtained from AlEt_2Cl and MgBu_2 is a particularly effective cocatalyst always yielding more polymer, of about the same stereospecificity, than the conventional aluminum trialkyls. The exact nature of the mixed metal alkyl cocatalysts is not known, but the available evidence argues against in situ aluminum trialkyl formation resulting from the alkylation of AlEt_2Cl by the second metal alkyl.

INTRODUCTION

The synthesis of high molecular weight poly- α -olefins, with high activity-supported Ti catalysts, is of great scientific and practical interest and has been the subject of many recent investigations.¹ Typical high activity catalysts, which produce more than 100,000 g polymer per gram of Ti, can be prepared by ball-milling anhydrous MgCl_2 with a Lewis base, for example, ethyl benzoate and impregnating the resulting finely divided solid with TiCl_4 . The final catalyst is obtained by mixing the MgCl_2 -supported TiCl_4 ($\text{MgCl}_2/\text{TiCl}_4$) with an aluminum trialkyl cocatalyst. Polymer stereospecificity, prepared with such a catalyst, is generally low (less than 50% isotactic polymer), but it can be increased by adding a Lewis base to the aluminum trialkyl.² Surprisingly AlEt_2Cl , which is the preferred cocatalyst in polymerizations employing nonsupported TiCl_3 , is a poor cocatalyst when used with $\text{MgCl}_2/\text{TiCl}_4$ and produces only low polymer yield and stereospecificity.

In the course of our work on α -olefin polymerization, we have observed that the cocatalyst activity of AlEt_2Cl can be greatly improved by the addition of a magnesium or lithium alkyl. The preparation of poly- α -olefins with such mixed metal alkyl cocatalysts in combination with $\text{MgCl}_2/\text{TiCl}_4$ is the subject of the present communication.

EXPERIMENTAL

Polymerizations were carried out in a 1-liter stainless steel autoclave. Before each run, the autoclave was heated to 120°C for 2 hours and cooled to room

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temperature in dry, oxygen-free nitrogen. Propylene (+99%) and 1-butene (+99%) were dried over silica gel, and *n*-hexane solvent was dried over molecular sieves (Linde 4A, 1/16-in. pellets). All operations were performed under nitrogen.

MgCl₂/TiCl₄ catalysts were synthesized according to procedures described in the patent literature. Catalyst designations used in the text are the following:

Catalyst	Composition	Ti, %	Reference
A	MgCl ₂ /EB/SiCl ₄ /TiCl ₄	1.90	3
B	MgCl ₂ /EB/EtOH/TiCl ₄	3.93	2
C	MgCl ₂ /EB/O-Cresol/TiCl ₄	3.66	2
D	MgCl ₂ /EB/TiCl ₄	0.75	4
E	MgCl ₂ /Durene/TiCl ₄ · EB	3.05	5

Abbreviations: Et = ethyl; Bu = butyl; i-Bu = isobutyl; Hex = hexyl; EB = ethyl benzoate.

Isotactic index (II), the weight percent of insoluble polymer in boiling *n*-heptane (polypropylene) or ether (poly-1-butene), was determined by Soxhlet extraction (6 h). Specific viscosity was measured in decalin (*c* = 0.1 g/100 mL) at 135°C (polypropylene) or 115°C (poly-1-butene).

RESULTS AND DISCUSSION

High Activity, Low Stereospecificity Mixed Metal Alkyl Cocatalysts

Polymerization experiments using a high activity MgCl₂/TiCl₄ catalyst and various metal alkyl cocatalysts are summarized in Table I. As expected,

TABLE I
Effect of Cocatalyst in Propylene and 1-Butene Polymerization

Cocatalyst	mM	g Polymer/g Ti	II	η _{sp} /C
Propylene^a				
AlEt ₂ Cl	1.4	17,000	22	1.0
AlEtCl ₂	1.4	0		
MgBu ₂	0.7	850		
AlEt ₃	1.4	132,000	48	2.4
Al(<i>i</i> -Bu) ₃	1.4	202,000	40	1.6
AlEt ₂ Cl/MgBu ₂	1.4/0.7	207,100	50	1.6
AlEtCl ₂ /MgBu ₂	1.4/1.4	39,000	59	2.2
AlEtCl ₂ /MgBu ₂	1.4/0.7	114,000	40	1.8
1-Butene^b				
AlEt ₂ Cl	5.6	300		3.0
AlEtCl ₂	5.6	0		
MgBu ₂	2.8	0		
Al(<i>i</i> -Bu) ₃	5.6	20,800	68	5.6
AlEt ₂ Cl/MgBu ₂	5.6/2.8	79,000	40	2.5
AlEtCl ₂ /MgBu ₂	5.6/5.6	25,200	52	2.4

^a163 g *n*-hexane, 125 g propylene, 0.59 mg Ti (Catalyst A), 50°C, 3 h.

^b66 g *n*-hexane, 220 g 1-butene, 2.6 mg Ti (Catalyst B), 25°C, 1 h.

TABLE II
 Polymerization of Propylene with Mixed Metal Alkyl Cocatalysts^a

Cocatalyst	mM	g Polymer/g Ti	II	η sp/C
AlEt ₂ Cl	1.4	17,000	22	1.0
AlEt ₂ Cl/MgBu ₂	1.4/0.7	207,000	50	1.6
AlEt ₂ Cl/MgHex ₂	1.4/0.7	47,500	55	2.4
AlEt ₂ Cl/LiBu	1.4/1.4	146,000	52	1.5
AlEt ₂ Cl/ZnEt ₂	1.4/0.7	3,400		
AlEt ₂ Cl/BEt ₃	1.4/0.7	11,900		2.3
Al(i-Bu) ₃	1.4	202,000	40	1.6
Al(i-Bu) ₃ /MgBu ₂	1.4/0.7	15,300	80	1.4
Al(i-Bu) ₃ /MgHex ₂	1.4/0.7	0		
Al(i-Bu) ₃ /LiBu	1.4/1.4	Trace		
AlEt ₃	1.4	132,400	48	2.4
AlEt ₃ /MgBu ₂	1.4/0.7	8,500		2.7

^a163 g *n*-hexane, 125 g propylene, 0.59 mg Ti (Catalyst A), 50°C, 3 h.

the aluminum trialkyls are good cocatalysts and produce high yields of polypropylene and poly-1-butene. When the same MgCl₂/TiCl₄ catalyst is used in conjunction with AlEt₂Cl, considerably less polymer is formed. With AlEtCl₂, no polymer is obtained, and MgBu₂ produces only a trace amount of polypropylene but no poly-1-butene. On the other hand, mixtures of alkylaluminum halides and magnesium alkyls form highly active cocatalysts. The mixed metal alkyl cocatalyst AlEt₂Cl + MgBu₂ is particularly effective and gives higher polymer yields than the conventional aluminum trialkyls. AlEtCl₂ + MgBu₂, although somewhat less effective, is also a good cocatalyst.

Other effective mixed metal alkyl cocatalysts are AlEt₂Cl + Mg(Hex)₂ and AlEt₂Cl + LiBu. The combinations AlEt₂Cl + ZnEt₂ or AlEt₂Cl + BEt₃ are inactive; and surprisingly aluminum trialkyls, which by themselves are good cocatalysts, are deactivated by Mg or Li alkyls (Table II).

High Activity, High Stereospecificity Mixed Metal Alkyl Cocatalysts

The superiority of AlEt₂Cl + MgBu₂ cocatalyst over the aluminum trialkyls was also demonstrated in polymerizations aimed to produce polypropylene of high isotactic content (Table III). In these experiments, the cocatalyst was mixed with ethyl benzoate (EB) as suggested in Ref. 2. The

 TABLE III
 Polymerization of Propylene with Ethyl Benzoate-Modified Cocatalysts^a

Cocatalyst	mM	g Polymer/g Ti	II	η sp/C
AlEt ₂ Cl/MgBu ₂ /EB	1.4/0.7/0.47	200,300	92	4.4
Al(i-Bu) ₃ /EB	1.4/0.47	120,500	91	4.3
AlEt ₃ /EB	1.4/0.47	157,900	86	3.1

^a163 g *n*-hexane, 125 g propylene, 0.59 mg Ti (Catalyst A), 50°C, 3 h.

TABLE IV
 Polymerization of Propylene with $\text{AlEt}_2\text{Cl}/\text{MgBu}_2/\text{EB}$ Cocatalyst Effect of EB Concentration^a

EB mM	g Polymer/g Ti			II	η_{sp}/C
	Total	Isotactic	Atactic		
0	207,100	103,600	103,600	50	1.6
0.23	195,200	166,000	31,200	84	1.1
0.47	200,300	184,300	16,000	92	4.4
0.64	166,400	156,400	10,000	94	3.8
0.94	103,600	101,500	2,100	98	5.2
1.26	30,600	30,300	300	99	5.5

^a163 g *n*-hexane, 125 g propylene, 0.59 mg Ti (Catalyst A), 1.4 mM AlEt_2Cl , 0.7 mM MgBu_2 , 50°C, 3 h.

data show that both polymer yield and isotactic content is greater with $\text{AlEt}_2\text{Cl} + \text{MgBu}_2$ than with the aluminum trialkyl cocatalyst.

At constant $\text{MgCl}_2/\text{TiCl}_4$ and mixed metal alkyl cocatalyst concentration, the polymer yield decreases and the isotactic polymer content increases with EB concentration (Table IV); but at all EB to Al ratios investigated, the polymer yield is greater with $\text{AlEt}_2\text{Cl} + \text{MgBu}_2$ than with $\text{Al}(i\text{-Bu})_3$ (Fig. 1).

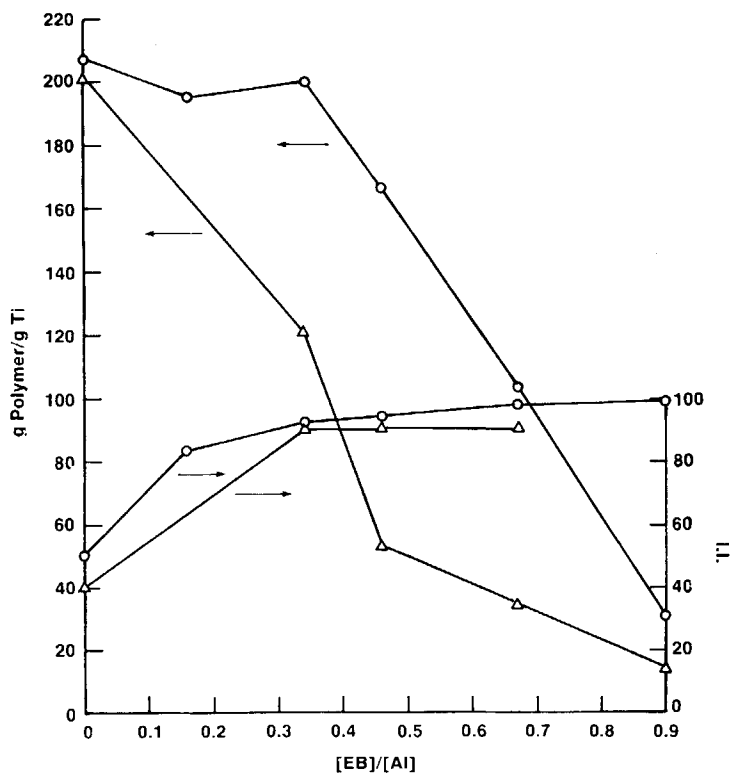


Fig. 1. Comparison of (○) $\text{AlEt}_2\text{Cl}/\text{MgBu}_2/\text{EB}$ and (Δ) $\text{Al}(i\text{-Bu})_3/\text{EB}$ cocatalysts in propylene polymerization. 163 g *n*-Hexane, 125 g Propylene, 0.59 mg Ti (Catalyst A), 1.4 mM $\text{AlEt}_2\text{Cl} + 0.7$ mM MgBu_2 (or 1.4 mM $\text{Al}(i\text{-Bu})_3$), 50°C, 3 h.

TABLE V
 Comparison of Mixed Metal Alkyl and Aluminum Trialkyl Cocatalysts in Propylene Polymerization

Cocatalyst	mM	Catalyst	g Polymer/g Ti	II	η sp/C
AlEt ₂ Cl/MgBu ₂ /EB	1.4/0.7/0.47	A ^a	200,000	92	3.4
Al(i-Bu) ₃ /EB	1.4/0.47	A ^a	120,000	91	4.3
AlEt ₂ Cl/MgBu ₂ /EB	5.6/2.8/1.9	B ^b	27,000	92	3.0
Al(i-Bu) ₃ /EB	5.6/1.9	B ^b	16,000	87	2.8
AlEt ₂ Cl/MgBu ₂ /EB	1.4/0.7/0.47	C ^c	69,000	85	2.7
Al(i-Bu) ₃ /EB	1.4/0.47	C ^c	32,000	86	3.0
AlEt ₂ Cl/MgBu ₂ /p-CH ₃ O-EB	1.0/0.5/0.29	D ^d	116,000	91	
AlEt ₃ /p-CH ₃ O-EB	1.0/0.29	D ^d	78,000	92	
AlEt ₂ Cl/MgBu ₂ /p-CH ₃ O-EB	2.4/1.2/0.9	E ^e	63,000	93	
AlEt ₃ /p-CH ₃ O-EB	2.4/0.9	E ^e	30,000	94	

^a163 g *n*-hexane, 125 g propylene, 0.59 mg Ti, 50°C, 3 h.

^b66 g *n*-hexane, 120 psi propylene, 2.6 mg Ti, 50°C, 3 h.

^c172 g *n*-hexane, 120 psi propylene, 0.92 mg Ti, 50°C, 3 h.

^d125 g *n*-hexane, 125 g propylene, 0.64 mg Ti, 50°C, 3 h.

^e50 g *n*-hexane, 290 g propylene, 1.3 mg Ti, 65°C, 5 h.

The amount of atactic polymer decreases monotonically whereas that of the isotactic polymer goes through a maximum as the concentration of EB is increased (Table IV). This is consistent with the suggestion that EB converts some of the atactic catalyst sites to isotactic ones.⁶ Variation of the Al to Mg ratio from 2 to 4 has little effect on polymer yield and stereospecificity, but at (Al)/(Mg) = 1, the polymer yield decreases substantially.

Experiments comparing mixed metal alkyl cocatalysts with aluminum trialkyls in propylene polymerization using various MgCl₂/TiCl₄ catalysts are shown in Table V. The results show, that with a broad range of MgCl₂/TiCl₄ catalysts, AlEt₂Cl + MgBu₂ produces always more polymer of about the same isotacticity than the conventional aluminum trialkyl cocatalyst.

Nature of Mixed Metal Alkyl Cocatalysts

The exact nature of mixed metal alkyl cocatalysts is unknown. When 2 mol of AlEt₂Cl is reacted with 1 mol of MgBu₂ in *n*-hexane, a solid precipitate is formed, which after isolation, analyses for 21.7% Mg, 4.1% Al, and 50.3% Cl (the balance is probably made up of alkyl residues). Thus the reaction is not simply the alkylation of AlEt₂Cl by MgBu₂ to give AlEt₂Bu and MgCl₂.⁷ Consequently, the high cocatalyst activity of mixed metal alkyls is not caused by the in situ conversion of the inactive AlEt₂Cl to an active aluminum trialkyl. Other experimental observations which rule out aluminum trialkyl formation are that AlEt₂Cl + MgBu₂ is always more active than AlEt₃ or Al(i-Bu)₃; and that AlEtCl₂ + MgBu₂ (mol ratio = 2/1) is also an active cocatalyst (Table I) even though the number of alkyl groups present is insufficient to give an aluminum trialkyl.

With AlEt₂Cl + MgBu₂, maximum cocatalyst activity is obtained when both the solid and liquid reaction products are present. Separation of the solid precipitate by filtration, using the clear filtrate results in a less active cocatalyst (Table VI).

TABLE VI
 Polymerization of Propylene with AlEt₂Cl/MgBu₂/EB Cocatalyst and Its Filtrate^a

Cocatalyst	mM	g Polymer/g Ti	II	η sp/C
AlEt ₂ Cl/MgBu ₂ /EB	2.8/1.4/0.94	90,000	92	4.0
Filtrate of: AlEt ₂ Cl/MgBu ₂ /EB	2.8/1.4/0.94	44,000	95	5.6

^a51 g *n*-hexane, 216 g refinery C₃ gas (125 g propylene), 1.2 mg Ti (Catalyst A), 50°C, 3 h.

The surprising deactivation of aluminum trialkyls by magnesium or lithium alkyls is not well understood. It may be caused by the formation of stable, oligomeric magnesium alkyl–aluminum alkyl complexes⁷ which are incapable of generating catalytically active Ti–alkyl sites.

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