SYMPOSIUM ON NOVEL PREPARATION AND CONVERSION OF LIGHT OLEFINS
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
MIAMI BEACH MEETING, SEPTEMBER 10-15, 1989

CONCURRENT DIMERIZATION AND POLYMERIZATION OF ETHYLENE USING NOVEL TITANIUM-MAGNESIUM CATALYSTS

By

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INTRODUCTION

The fact that ethylene can be selectively dimerized to butene-1 as well as polymerized to polyethylene over titanium-aluminum catalysts has resulted in many attempts to design a single dual ~~functional catalyst capable of~~ concurrently dimerizing and polymerizing ethylene to branched co-polymers (1). Many of these catalyst compositions consist of a halogen-containing titanium compound, optionally on a support, as a polymerization centre and an alkoxy bearing titanium compound as a centre for dimerization. However, in view of the known propensity of chlorine-alkoxy ligand exchange reactions, the two centres are far from being distinct and chemically non-interfering.

In our effort to devise a chemically compatible and yet non-interfering dual functional catalyst, we initially examined magnesium chloride-titanium-n-butoxide (TNB) in combination with TNB. We reasoned that $MgCl_2$-TNB catalyst would function as a polymerization centre (2) whereas free TNB would act as a dimerization centre in conjunction with triethylaluminum. The study led to the discovery that $MgCl_2$-TNB catalysts depending on the Mg:Ti ratio can show a range of activity from selective dimerization to polymerization of ethylene. This fact was used to devise a novel dual functional catalyst for concurrent dimerization and copolymerization of ethylene.

EXPERIMENTAL

All manipulations involving catalysts were carried out in an inert atmosphere box under a continuous stream of ultra high purity nitrogen (moisture and oxygen < 5 ppm). Anhydrous magnesium chloride (M/s.Toho Titanium Co. Tokyo, Mg = 25.49%, Cl = 74.4%, H_2O = 0.05%, surface area 82 M^2/g) and triethylaluminum (Ethyl Corporation, USA) were used as received. TNB (Synthochem, India) was purified by vacuum distillation followed by azeotropic removal of free butanol with cyclohexane. Solvents (n-heptane, C_{11}-C_{14} paraffins) were refluxed over sodium wire and freshly distilled before use.

Preparation of Mg-Ti catalysts

Anhydrous $MgCl_2$ (1 mole) was heated with just sufficient amounts of TNB at 125°C to effect complete dissolution of the $MgCl_2$.

The resultant homogeneous solution analyzed for the composition $MgCl_2$ $[TNB]_4$. Solid Mg-Ti catalyst was prepared by milling anhydrous $MgCl_2$ with excess TNB in a centrifugal ball mill for 24 hrs washed with excess boiling n-heptane to remove all free TNB and the filtrate dried in vacuo. The results of elemental analysis of catalysts are shown in Table I.

Dimerization and Polymerization

Ethylene dimerization studies were conducted using Et_3Al as a co-catalyst in a C_{11}-C_{14} paraffin solvent at 27°C and 1 atm C_2H_4 pressure using a method previously reported (4). Polymerization studies at 1 atm pressure were conducted in a glass cell connected to gas burette and an ethylene reservoir at 30°C in n-heptane as solvent.

TABLE I

MAGNESIUM-TITANIUM CATALYSTS-ANALYTICAL DATA

Catalyst Designation	Composition	State	% Mg	% Ti	% Cl	Mg/Ti Mole Ratio
A	$MgCl_2[TNB]_4$	Liquid	1.4	12.8	4.3	0.23
B	$MgCl_2[TNB]_{0.1}$	Solid	19.4	5.2	54.6	9.06

Analysis

Dimerization products were analyzed by GC using a 2% $AgNO_3$ + 15% PEG 20M column, temperature 60-190%, FID, H_2=20 mL min^{-1}. Ethyl branching in polymers was analyzed using FT-IR spectroscopy using a SRF-1475 NBS standard linear polyethylene as a reference sample and the methyl symmetrical deformation bands around 1378 cm^{-1} (5). Tm was determined using a DSC (DuPont 910), heating rate 10°C min^{-1}, N_2; 100 mL min^{-1}.

RESULTS AND DISCUSSION

Anhydrous $MgCl_2$ dissolves in neat titanium-n-butoxide (4 moles TNB per mole of $MgCl_2$) at 125°C to form a homogeneous solution. Neat TNB exists as a tetramer wherein the two internal titanium atoms are coordinatively unsaturated (CN=5). It is proposed that the dissolution of $MgCl_2$ is favored by the complexation of the chloride ligand with the vacant coordination site on titanium, forming a stoichiometric complex $MgCl_2$. $[TNB]_4$ (catalyst A). This complex was found to be active in selective dimerization of ethylene. Data on initial rates, conversion and selectivity along with comparative results obtained with a TNB catalyst containing no $MgCl_2$ is shown in Table II. In general the Mg-Ti catalyst is characterized by high initial rates but low overall conversion. For Mg free catalyst, selectivity remains unchanged over a range of Al/Ti ratios (5-100). On the contrary the Mg-Ti catalyst show an initial decrease in selectivity (up to Al/Ti = 50) followed by sharp increase in selectivity (95% butene-1) at Al/Ti = 100. No solid polymer was formed in any of the experiments.

TABLE II

COMPARATIVE RESULTS OF ETHYLENE DIMERIZATION CATALYZED BY $MgCl_2[TNB]_4$ - Et_3Al and TNB - Et_3Al SYSTEMS[a]

Sr. No.	Al/Ti Mole Ratio	Conversion %	Initial Rate mol(C_2H_4) min^{-1} atm^{-1}	Product Distribution, % Butene-1	3Me Pentene-1	2 Et Butene-1	C_8 Oligomers
$MgCl_2[TNB]_4$							
1	5	68	6.7	89	6	2	3
2	10	66	5.2	79	6	7	8
3	50	45	1.9	44	18	26	12
4	100	20	1.7	95	1	2	2
TNB							
5	5	96	3.9	79	6	11	4
6	10	88	1.5	79	7	13	1
7	50	41	2.0	83	12	3	2
8	100	39	0.9	79	11	1	9

[a] Temperature: 27 ± 2°C, Reaction Time= 45 min., C_2H_4 = 1 atm, Solvent = 100 mL C_{11}- C_{14} hydrocarbon

In contrast, solid Mg-Ti catalysts with higher Mg/Ti ratios promote ethylene polymerization. The results with catalyst B are shown in Table III. Analysis of vapor phase by GC showed no formation of butene-1 indicating that catalyst B is selective for polymerization. Catalyst B also showed high activity (200 kg PE/gTi, 70°C, 2hr C_2H_4 10 atm) even at low Al/Ti ratios (<100). Furthermore the polymerization showed a relatively slower rate decay. These observations are generally in agreement with those reported in the literature (2).

TABLE III

ETHYLENE POLYMERIZATION $MgCl_2[TNB]_{0.1}$-Et_3Al CATALYST[a]

Sr. No.	Al/Ri Mole Ratio	Conversion %	Catalyst Productivity gPE-gTi^{-1}
1	10	77	80
2	25	85	88
3	45	85	98
4	100	83	101
5	200	81	109

[a] Temperature: 30°C, Reaction Time: 2hr, C_2H_4 = 1 atm, n-heptane

The concurrent dimerization-polymerization of ethylene was therefore attempted by a suitable blend of catalyst A and B. The results are shown in Table IV. Best results were achieved when TEAL/catalyst A was added first to the reaction vessel, allowed to react for 10 min followed by addition of catalyst B as a heptane slurry. Ethyl branching (butene-1 incorporation) was found to increase with increasing molar ratio of catalyst A:B. However, compared to prior results (lb, d) the loss in catalyst productivity was less than 15% over a broad range of butene-1 incorporation. Apparently, the present catalyst system is prone to much less poisoning by the individual catalyst components. Control experiments established that there was no major change in catalyst composition when catalyst A and B were mixed in n-haptane indicating that the catalyst complexes had no liable ligands capable of undergoing exchange.

TABLE IV

CONCURRENT DIMERIZATION AND POLYMERIZATION OF ETHYLENE ON Mg-Ti-Al CATALYSTS[a]

Sr.No.	$\frac{[\text{Catalyst A}]}{[\text{Catalyst B}]}$ Molar Ratio	Catalyst Productivity gPE. gTi^{-1}	Butene-1 in Polymer[c], mole %	Tm, °C[d]
1	-[a]	100	-	138
2	0.5	93	1.8	132
3	1.5	90	2.6	128
4	3.5	86	4.8	124

[a] Temperature 30°C , Reaction Time: 2hr, Solvent n-heptane, Al/Ti = 100, C_2H_4 = 1 atm Catalyst: Triethylauminum;

[b] Pure TNB ; [c] BY IR ; [d] by DSC

CONCLUSIONS

1. Mg-Ti catalysts consisting of $MgCl_2$ and Ti(n-OBu)$_4$ show a range of activity from selective dimerization to polymerization of ethylene depending on Mg/Ti ratios.
2. Appropriate blends of catalysts result in concurrent dimerization and copolymerization of ethylene.
3. The two catalyst types are chemically similar and have no labile ligands capable of migrating from one centre to another causing poisoning of one or the other centre. This is reflected in less than 15% reduction in catalyst productivity over of a range of butene-1 incorporated in polyethylene.
4. The catalyst systems described in this paper are novel in the sense that they consist of only one titanium compound, i.e. Ti(n-OBu)$_4$, yet are capable of two distinct functions. Presumable the two active centres differ only in the nature of the electronic environment surrounding titanium.

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