Synthesis, characterization and polymerization of ethylene using a novel soluble magnesium–titanium catalyst*

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A 1:2 complex of $MgCl_2$ and tetrahydrofuran (THF) was prepared by a simple Grignard decomposition reaction using Mg metal and 1,2-dichloroethane in THF as diluent. The $MgCl_2.2THF$ complex formed a homogeneous solution with titanium-n-butoxide in xylene at 60°C. The soluble Mg–Ti complex in xylene polymerized ethylene under homogeneous conditions in the presence of organoaluminium compounds. The kinetic behaviour of the polymerization reaction was studied. It was observed that the presence of $MgCl_2$ transformed the Ti centre from a dimerization to a polymerization catalyst.

(Keywords: magnesium chloride; titanium-n-butoxide; magnesium–titanium catalyst)

INTRODUCTION

Solid catalysts based on anhydrous $MgCl_2$ and Ti halides have attracted considerable attention during the past decade as components of high efficiency ethylene and propylene polymerization catalysts[1]. The role of $MgCl_2$ in these catalysts has been widely discussed in the literature[2]. There are, however, only a few reports of truly soluble Mg–Ti catalysts for olefin polymerization. Soga *et al.* prepared a soluble metal halide–2-ethylhexanol complex which, in conjunction with titanium-n-butoxide and diethylaluminium chloride, polymerized propylene[3]. This catalyst enabled the authors to study the effect of the electronegativity of the metal in the metal halide on catalyst activity. Yano *et al.* prepared a $MgCl_2$–2-ethylhexanol complex which, in conjunction with $TiCl_4$ or titanium-n-butoxide and diethylaluminium chloride, was used as a catalyst for high temperature polymerization of ethylene[4,5]. In both of these studies, whereas the precursors were hydrocarbon soluble, the true catalyst formed by the addition of diethylaluminium chloride was heterogeneous.

More recently, truly soluble Mg–Ti catalysts have been reported by Makino *et al.*[6,7] and Zucchini *et al.*[8–10]. Reduction of $TiCl_4$ by Grignard reagent or solubilizing anhydrous $MgCl_2$ with trialkylphosphate was reported to result in soluble Mg–Ti catalysts capable of copolymerizing ethylene with propylene[6,7]. Reaction of anhydrous $MgCl_2$ with titanium-n-ethoxide in a 2:1 stoichiometry results in an isolable bimetallic complex capable of polymerizing ethylene in a homogeneous medium in toluene[8–10].

We have recently observed that a complex of anhydrous $MgCl_2$ with tetrahydrofuran (THF) prepared *in situ* from a Grignard decomposition reaction forms a soluble complex with titanium-n-butoxide, which in conjunction with organoaluminium compound initiates ethylene polymerization under homogeneous conditions in xylene as the solvent[11]. This paper reports our results on the synthesis, characterization and polymerization of ethylene using this novel soluble Mg–Ti catalyst.

EXPERIMENTAL

Materials

Magnesium turnings (Loba Chemicals, Bombay, India), triisobutylaluminium (TIBAL), diethylaluminium chloride (DEAC), triethylaluminium (TEAL), trimethylaluminium (TMA) and trioctylaluminium (TOAL) (all from Schering AG, Bergkamen, Germany) were used as received. 1,2-Dichloroethane (SD Fine Chemical, Bombay, India) was distilled over CaH_2 and stored over 3 Å molecular sieves. Polymer grade ethylene was obtained from the Gas Cracker Complex of the Indian Petrochemical Corporation Limited (Nagothane, India). It had a moisture content of <4 ppm (Shaw model SHA-TR moisture analyzer) and oxygen content of <3 ppm (Braun oxygen analyzer). Titanium tetra-n-butoxide (TNB; Synthochem, India) was vacuum distilled twice and was further purified by adding TIBAL (2 ml in 10 ml of hexane) to TNB (15 ml) dropwise at room temperature. The colour of the solution turned black. The mixture was stirred for 30 min and distilled at 120°C (0.5 mm Hg). Solvents were dried over CaH_2 and distilled over Na wire under a positive pressure of high purity N_2 or Ar. All manipulations involving air-sensitive compounds were performed inside a Labconco (model 50004) inert atmosphere glove box continuously purged with high purity N_2 (<5 ppm) generated using a N_2 generator (Spantech, model NG 300-1, UK) or under a positive pressure of high purity N_2 using standard bench-top inert atmosphere techniques.

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Synthesis of $MgCl_2$.2THF

A three-necked round-bottom flask equipped with a magnetic bar, N_2 inlet, addition funnel and a reflux condenser was flame dried and cooled under N_2 atmosphere. Iodine activated Mg turnings were placed in the flask and THF was added at 40°C. 1,2-Dichloroethane (30 ml) was added dropwise to the refluxing THF until all the Mg turnings dissolved. Evolution of ethylene indicating rapid decomposition of β-chloroethylmagnesium chloride and concomitant formation of a THF complex of $MgCl_2$ was observed. The solid was filtered and dried under vacuum for 8 h at 30°C (yield 16.5 g; Mg = 10.5%, Cl = 27.8%).

Preparation of soluble catalyst

$MgCl_2$.2THF (2 g) was placed in a three-necked round-bottom flask fitted with a condenser, N_2 inlet and a septum. Xylene (50 ml) was added in the flask followed by TNB (4 ml) using a hypodermic syringe. The slurry was heated at 60°C in an oil bath for 8 h with stirring. It was found that the solid slowly dissolved in the xylene phase. The reaction mixture was cooled. The unreacted $MgCl_2$.2THF was allowed to settle and the supernatant clear liquid was transferred by a cannula into an Aldrich Sure/Seal® bottle under N_2 pressure. The clear liquid was analysed for Ti (8.7 mg) and Mg (3.8 mg) in 1 ml of xylene solution.

Polymerization of ethylene

Polymerization was performed in a stirred glass cell at 1 atm (1×10^5 Pa) of ethylene in xylene and hexane as diluents. A gas burette with a reservoir containing silicone oil was used to feed ethylene continuously to the cell. The reaction cell was dried at 120°C overnight and cooled under N_2. Solvent was introduced into the cell using a hypodermic syringe followed by xylene soluble Mg–Ti catalyst (0.2 ml) with a hypodermic syringe. The solvent was saturated with ethylene. Polymerization was initiated by the addition of an organoaluminium compound. The reaction temperature was maintained by circulating water from a thermostat through the jacket of the cell and the gas burette. Ethylene uptake was measured as a function of time. The reaction was terminated after 30 min by addition of acidified methanol. The polymer was filtered and dried at 40°C under vacuum.

Analysis

Chlorine and magnesium estimation was performed by argentimetric and EDTA titrations, respectively. The Ti content in the catalyst was determined by the u.v. technique using a Hitachi (model 220) u.v.-visible spectrophotometer[12]. The n.m.r. spectrum of the support was recorded in D_2O using a Brüker FT-80 n.m.r. spectrometer. The Fourier transform infra-red (*FT*i.r.) spectrum of support was run on a Perkin–Elmer 16PC FT-IR in Nujol mull using NaCl cells (1600–400 cm^{-1}). The powder X-ray diffraction (XRD) was recorded on a Phillips PW 1730 spectrometer using Ni-filtered CuKα radiation. Thermogravimetric analysis (t.g.a.) was performed on a Perkin–Elmer TGA-7 thermal analysis work station. Surface area measurements were performed by Quantachrome mercury intrusion porosimetry. The e.s.r. spectrum was run on a Brüker (model ER-200D) e.s.r. spectrometer at room temperature (9.72 GHz). Differential scanning calorimetric analysis of polyethylene was performed on a Perkin–Elmer DSC-7 thermal analysis work station.

RESULTS AND DISCUSSION

Preparation of $MgCl_2$.2THF

The THF adduct of $MgCl_2$ was prepared by a single-step decomposition of Grignard reagent derived from Mg metal and 1,2-dichloroethane in THF at 60°C:

$$Mg + Cl\text{–}CH_2\text{–}CH_2\text{–}Cl \xrightarrow{THF, 60^\circ C} MgCl_2.2THF + C_2H_4$$

The solid complex precipitated out of solution. Although the facile decomposition of a Grignard reagent derived from Mg metal and 1,2-bromoethane is reported in the literature[13], the analogous reaction with 1,2-dichloroethane appears to have no precedent. Complexes of $MgCl_2$ with THF have been synthesized earlier by Handlir *et al.*[14] by the reaction of $HgCl_2$ and Mg metal in THF at 60°C. The complex isolated was observed to be insoluble in hexane or xylene even at refluxing temperatures.

Elemental analysis established the stoichiometry of the complex as $MgCl_2$.2THF. The presence of THF was established by the appearance of triplets at 3.7 and 5.7 ppm in the ^1H n.m.r. spectrum in D_2O as solvent and bands at 1039 and 885 cm^{-1} in the *FT*i.r. spectrum. The powder XRD spectrum of $MgCl_2$.2THF showed strong reflections at $2\theta = 29.2$, 32.4 and 40.8°. In comparison, anhydrous $MgCl_2$ (Toho Titanium Co., Tokyo, Japan) showed all the above reflections and also a noticeable reflection at $2\theta = 31.5°$ which is absent in $MgCl_2$.2THF. The powder XRD pattern of $MgCl_2$.2THF is in agreement with that reported in the literature but prepared by a different route[14]. The results show that the complex is highly crystalline. The complex had a total pore surface area of 10 $m^2 g^{-1}$ and a mean pore volume of 0.83 $cm^3 g^{-1}$. $MgCl_2$.2THF was subjected to t.g.a. (N_2 atmosphere, 50–300°C, rate of 10°C min^{-1}). The results showed that the THF loss occurred in a two-stage process. The total weight loss was observed to be 74% which corresponds to 2 mol of THF per mole of $MgCl_2$ (*Figure 1*).

Preparation of soluble Mg–Ti catalyst

Under defined experimental conditions, $MgCl_2$.2THF and TNB were found to be soluble in xylene at 60°C forming a homogeneous solution. The solution typically analysed for Ti and Mg, 8.7 and 3.8 mg ml^{-1}, respectively. However, upon addition of hexane a solid precipitated out which, after repeated washing with dry hexane,

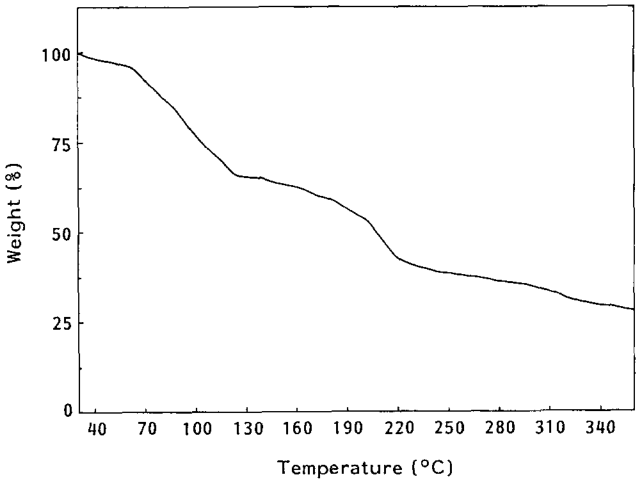

Figure 1 Thermogravimetry of $MgCl_2$.2THF

analysed for Ti and Mg, 0.2 and 1.0% per gram of isolated solid. This indicates that the complex existing in solution in xylene breaks into its component constituents in hexane. Our attempts to isolate the soluble complex free of xylene have so far been unsuccessful.

The xylene soluble Mg–Ti complex was estimated to contain 1.5 mol of TNB per mole of $MgCl_2.2THF$. The soluble catalyst showed on reduction with TIBAL a sharp intense signal at $g=1.94$ in the e.s.r. spectrum. The intensity of the signal was observed to be relatively higher than the signal obtained with the TNB-TIBAL catalyst system. The sharp intense signal without any fine structure indicates that the Mg–Ti catalyst is homogeneous in xylene.

Polymerization of ethylene

Ethylene polymerization was conducted using the soluble Mg–Ti catalyst in xylene and hexane as the reaction media at a total pressure of 1 atm. The results are shown in *Tables 1, 2* and *3*. Even upon addition of the organoaluminium cocatalyst, the Mg–Ti complex showed no evidence of precipitation in xylene. Catalyst activity was high with DEAC compared to trialkylaluminiums in xylene (*Table 1*). With DEAC as cocatalyst the conversion to polymer increased with temperature. The catalyst activity also increased with Al/Ti ratio. The catalyst activity was relatively poorer with trialkylaluminiums. No ethylene absorption was observed below an Al/Ti ratio of 100. Furthermore, polymerization activity decreased as the alkyl length in the organoaluminium compound increased (*Table 2*). In hexane, the catalyst precipitated as a fluffy, white material which also polymerized ethylene, but with reduced activity (*Table 3*). However, the polymer molecular weights were higher. The polyethylene obtained in all cases was observed to have a melting temperature of 135–140°C with the

Table 1 Polymerization of ethylene using soluble Mg–Ti catalyst in xylene[a]

Entry	Al/Ti wt ratio	Cocatalyst	Temp. (°C)	Conv. (%)	Activity (g PE g^{-1} Ti h^{-1})	$[\eta]$[b] (dl g^{-1})
1	12	DEAC	70	78	397	3.2
2	50	DEAC	70	80	522	2.5
3	100	DEAC	70	80	633	1.4
4	50	DEAC	50	60	355	2.3
5	50	DEAC	30	50	231	2.5
6	100	TIBAL	70	72	35	2.9
7	200	TIBAL	70	72	35	3.1
8	200	TIBAL	30	65	30	2.8
9	200	TIBAL	50	68	39	2.7
10	200	TIBAL	70	70	40	3.1

[a] Polymerizations were performed at a total pressure of 1 atm for 30 min

[b] Intrinsic viscosities were measured in *o*-dichlorobenzene at 135°C

Table 2 Polymerization of ethylene using soluble Mg–Ti catalyst in xylene. Effect of cocatalyst[a]

Entry	Al/Ti wt ratio	Cocatalyst	Temp. (°C)	Conv. (%)	Activity (g PE g^{-1} Ti h^{-1})	$[\eta]$[b] (dl g^{-1})
1	100	DEAC	70	80	633	1.4
2	100	TMAL	70	78	68	2.4
3	100	TEAL	70	75	50	2.2
4	100	TIBAL	70	72	35	2.4
5	100	TOAL	70	–	–	–

[a] Polymerizations were performed at a total pressure of 1 atm

[b] Intrinsic viscosities were measured at 135°C in *o*-dichlorobenzene

Table 3 Polymerization of ethylene using soluble Mg–Ti catalyst in hexane[a]

Entry	Al/Ti wt ratio	Cocatalyst	Temp. (°C)	Conv. (%)	Activity (g PE g^{-1} Ti h^{-1})	$[\eta]$[b] (dl g^{-1})
1	12	DEAC	30	82	235	4.5
2	50	DEAC	30	80	275	4.3
3	100	DEAC	30	90	310	4.0
4	100	TIBAL	30	78	224	3.9
5	200	TIBAL	30	85	210	4.2

[a] Polymerizations were performed at a total pressure of 1 atm

[b] Intrinsic viscosities were measured at 135°C in *o*-dichlorobenzene

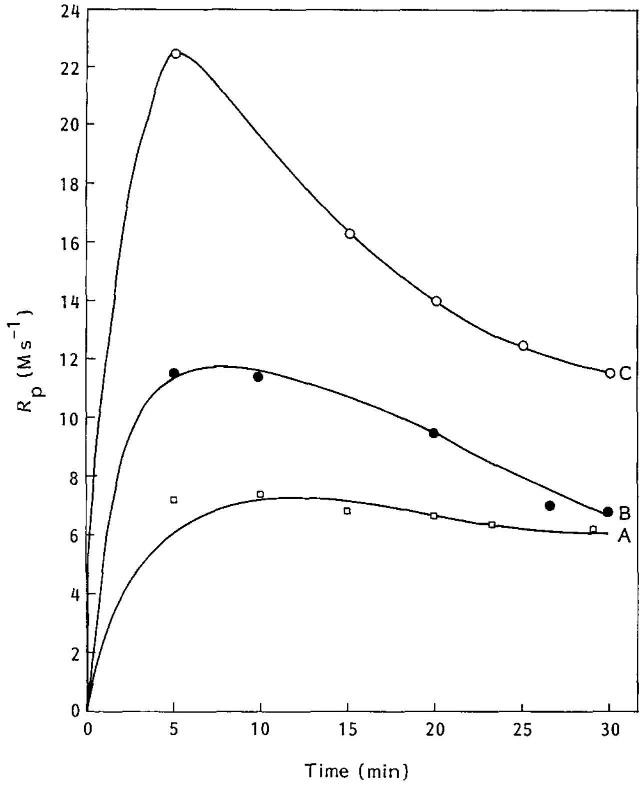

Figure 2 Plot of the rate of polymerization *versus* time for the Mg–Ti/DEAC catalyst system. [Ti] = 3.6 × 10^{-5} mol. Al/Ti: (A) 12; (B) 50; (C) 100

percentage of X-ray crystallinity varying between 60% and 70%.

A kinetic investigation of ethylene polymerization on xylene soluble Mg–Ti catalyst was conducted. A plot of the rate of polymerization (R_p) *versus* time (*Figure 2*) showed a steady-state kinetic curve at low Al/Ti ratio or temperature up to 50°C in xylene medium. At temperatures above 50°C and with Al/Ti >50, the kinetic plots progressively changed into a decay-type curve indicating a competing deactivation process. The Arrhenius plot of $\log R_p$ *versus* time was linear with an overall activation energy of 3–4 kcal mol^{-1} (13–17 kJ mol^{-1}). This value is similar to that observed for homogeneous catalysts in the Group IV metallocene–aluminoxane system[15].

TNB in conjunction with organoaluminium compounds is known to promote only selective dimerization of ethylene to butene-1[16]. We reported earlier that a soluble $MgCl_2$.TNB complex (Mg/Ti = 0.23) can be obtained by a thermochemical reaction of TNB and anhydrous $MgCl_2$ which promoted selective dimerization of ethylene to butene-1[17]. In contrast, the soluble Mg–Ti catalyst (Mg/Ti = 0.38) promoted ethylene polymerization to a high molecular weight linear polyethylene. The results are best understood in terms of bimetallic species formed by the cleavage of the distorted orthorhombic structure of $MgCl_2$.2THF[18] by the tetrameric TNB. The chlorine ligands of $MgCl_2$ thus contribute to the stability of the Ti–C bond resulting in the polymerization activity. Thus, in these catalyst systems, $MgCl_2$ exerts a subtle yet significant influence on the nature of the Ti active centre in transforming it from a dimerization to a polymerization catalyst.

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