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Preparation of soluble $TiCl_4$ catalyst modified with some metal chlorides and its use for ethylene and propylene homopolymerization

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Polymerizations of ethylene or propylene were conducted in toluene employing the soluble catalytic system $TiCl_4.THF/AlCl_2(C_2H_5)/Al(i\text{-}C_4H_9)_3$ combined with different metal chlorides ($CoCl_2$,$MgCl_2$ or $ZnCl_2$) complexed with tetrahydrofuran (THF). The catalyst activity was strongly dependent upon the metal chloride used as modifier. A clear increase of catalyst activity in ethylene polymerization was observed when the Co/Ti or Mg/Ti mole ratio was increased up to 2 and then decreased markedly. In a similar way, the catalyst activity in propylene polymerization was strongly dependent upon the amount and kind of metal chloride used as modifier.

(Keywords: Ziegler–Natta catalyst; homopolymerization; soluble catalyst)

Introduction

A previous publication[1] reported preliminary results on the polymerization of ethylene and/or propylene employing the catalyst $SiO_2/TiCl_4/MgCl_2$ activated by $Al(i\text{-}C_4H_9)_3$; there was an increase of catalyst activity for ethylene and/or propylene polymerizations when $MgCl_2$ was used as catalyst modifier. Recently, ethylene and propylene homopolymerizations were carried out using the homogeneous catalyst based on $TiCl_4$ complexed with tetrahydrofuran (THF) and modified with metal chlorides ($CoCl_2$, $MgCl_2$ or $ZnCl_2$) also complexed with THF in toluene solution. It was found that when the metal chloride used was $MgCl_2$ or $CoCl_2$, the catalyst activity increased markedly. On the other hand, the use of $ZnCl_2.2THF$ as catalyst modifier caused a decrease of the activity for both ethylene and propylene polymerizations.

In many papers[2–5], Soga *et al.* have discussed the influence of metal chloride on different catalyst systems and have shown that the catalyst activity is dependent on the electronegativity of the metal ion in the metal chloride. This fact encourages the development of a catalyst with enhanced activity for ethylene and/or propylene polymerizations by modifying the soluble catalyst based on $TiCl_4$ with suitable metal chlorides.

This paper deals with the results of ethylene and propylene homopolymerizations together with the method of catalyst preparation.

Experimental

Materials. Research grade ethylene, propylene, THF and toluene were purified according to the usual methods[6]. Nitrogen of ultrahigh purity (from Nippon Sanso Co.) was purified by passing through a molecular sieve. The other chemicals (research grade) were purchased from commercial sources and used without further purification.

Catalyst preparation. To a $100\,cm^3$ glass reactor or an autoclave ($100\,cm^3$ capacity) equipped with a magnetic stirrer were added $50\,cm^3$ of toluene, and certain amounts of $TiCl_4.THF$ in toluene solution (0.01 mmol of Ti) and $MtCl_2.THF$ in toluene solution under nitrogen. The mixture was kept standing with vigorous stirring for 10 min at room temperature (r.t.). To this mixture was added $AlCl_2(C_2H_5)$ in toluene solution and the resulting mixture was kept standing with vigorous stirring for 10 min at 0°C.

Ethylene and propylene polymerization procedures. To the above mixture was added $Al(i\text{-}C_4H_9)_3$ in toluene solution. The reactor was then degassed, followed by introduction of ethylene until saturation at atmospheric pressure. The ethylene was fed continuously during the polymerization time (10 min) at 0°C. The propylene polymerization was performed in a $100\,cm^3$ autoclave equipped with a magnetic stirrer. After the addition of $Al(i\text{-}C_4H_9)_3$ in toluene solution, a measured amount of monomer (7 l) was introduced at liquid nitrogen temperature. The polymerization reaction was terminated by adding a dilute hydrochloric acid solution in methanol. The precipitated polymer was washed with methanol several times, followed by drying *in vacuo* at 60°C for 6 h.

Analytical procedures. The ^{13}C n.m.r. spectra of the polymers were measured at 120°C using a Jeol FX-100 spectrometer operating at 25.047 MHz. The solution was made in trichlorobenzene up to 15% w/v. The chemical shift was represented in ppm downfield from the internal hexamethyldisilane (HMDS).

Results and discussion

It is well known that the activity of Ziegler–Natta catalysts is enhanced substantially by using metal chlorides as carriers for titanium compounds, the most common one being $MgCl_2$. In the literature, the increase in the propagation rate constant has been attributed to two causes: the increase of catalyst site population, and the formation of a bimetallic complex between titanium compounds and magnesium chloride which is stable and more active for olefin polymerization[7–9].

Soga and co-workers[1–4] developed a catalyst based on $TiCl_4$ supported on SiO_2 and modified with $MgCl_2$, and also studied the influence of other metal chlorides on the performance of Ziegler–Natta catalysts. As well as being of industrial importance, the catalyst gives some clues as to why $MgCl_2$ markedly accelerates the propagation rate constant of this kind of catalyst. It would be expected, therefore, that a high level of polymerization of olefin could be conducted with a soluble catalyst system based on $TiCl_4$ modified by $MtCl_2$ in an appropriate medium.

Ethylene polymerization. The polymerization of ethylene with $TiCl_4$ complexed with THF and solubilized in toluene using $Al(i\text{-}C_4H_9)_3$ (TIBA) as cocatalyst was examined. $TiCl_4$ complexed with THF was not able to polymerize ethylene by activation with TIBA. The catalyst system was active only when $AlCl(C_2H_5)_2$, $Al_2Cl_3(C_2H_5)_3$ or $AlCl_2(C_2H_5)$ were employed as Lewis acids to form a soluble complex among the catalyst components in appropriate conditions. The ether may have complexed the titanium catalyst species, preventing the polymerization process. Among the alkyl chlorides employed as Lewis acids, ethylaluminium dichloride was chosen for its low reduction power in relation to other aluminium alkyls, avoiding the reduction of titanium species by the Lewis acid.

The effect of metal chlorides on the activity of $TiCl_4$ catalyst in ethylene polymerization is summarized in *Table 1*. With an increase in the mole ratio of Mg/Ti or Co/Ti, the activity was greatly enhanced, attaining a maximum value at a mole ratio of about 2, as Soga *et al.*[2–4] found. On the other hand, Doi *et al.*[10] found a constant value after having reached the maximum value. The excess THF may have poisoned the catalyst sites. For the catalyst modified with zinc chloride, the catalyst activity was lower than that of the unmodified catalyst. This behaviour has been attributed to the influence of metal chloride on the bimetallic complex formation between the titanium site and the other metal. The ability of metal chlorides for electron-donating or electron-withdrawing is likely to modify the coordination of a monomer molecule with Ti^{3+}, depending on their electronegativities compared to Ti^{3+}. If the back-donation of an electron from Ti^{3+} to the monomer is the main factor in the interaction of the Ti–monomer complex, the metal chloride should have a favourable effect or no effect on the subsequent insertion of the coordinated monomer into the active Ti–polymer chain bond[5].

Table 1 Results of ethylene polymerization[a]

Polymerization no.	Type of $MtCl_2$	Mt/Ti mole ratio	Polymer yield (g)
1	–	–	0.14
2	$MgCl_2$	1.0	1.48
3		2.0	2.80
4		2.5	2.00
5		3.0	1.40
6	$CoCl_2$	1.0	1.40
7		2.0	3.40
8		2.5	2.48
9		3.0	1.40
10	$ZnCl_2$	1.0	trace
11		2.0	trace
12		3.0	no result

[a] Polymerization was conducted in a glass reactor at 0°C for 10 min by using 0.01 mmol of Ti, 50 cm^3 of toluene, 0.01 mmol of $Al(i\text{-}C_4H_9)_3$, ethylene at atmospheric pressure

Table 2 Results of propylene polymerization[a]

Polymerization no.	Type of $MtCl_2$	Mt/Ti mole ratio	Polymer yield (g)	Al/Ti mole ratio
13	–	–	0.13	1
14	–	–	0.59	2
15	–	–	0.35	5
16	–	–	0.10	10
17	$MgCl_2$	1	1.78	2
18		2	3.68	2
19		3	0.38	2
20	$CoCl_2$	1	0.89	2
21		2	4.60	2
22	$ZnCl_2$	1	trace	2

[a] Polymerization was conducted in an autoclave of 100 cm^3 capacity at 40°C for 24 h using 0.01 mmol of Ti, 7 l of propylene at atmospheric pressure, and 50 cm^3 of toluene

Propylene polymerization. Propylene polymerization was conducted with the same catalyst systems and the results are shown in *Table 2*. The catalyst systems were activated by $AlCl_2(C_2H_5)$ addition, as for the ethylene polymerization. The effect of metal chloride on catalyst activity during propylene polymerization was the same as for ethylene polymerization. The catalyst activity was substantially enhanced by the use of metal chloride as catalyst modifier. The best value of Mt/Ti mole ratio seems to be 2, as seen in *Table 2* (polymerization 18). The employment of $ZnCl_2$ deactivated the catalyst system (polymerization 22). The polypropylene stereoregularity was dependent on the use of a modifier. The ^{13}C n.m.r. spectrum of the polymer obtained with unmodified catalyst (polymerization 14) was predominantly atactic polypropylene ($mr = 80\%$). On the other hand, the polymers obtained with modified catalysts by $MgCl_2$ or $CoCl_2$ (polymerizations 18 and 21) presented higher values of tacticity ($mm = 35\%$ and $mm = 38\%$, respectively). It is therefore possible to explain these results by the larger hindrance of the bimetallic complex formed between $TiCl_4$ and $MgCl_2$ which may have a favourable effect on isotactic polymerization. However, a more detailed study on the characterization of the catalyst is necessary to speculate on the active sites of $MtCl_2$-modified catalyst.

In conclusion, the homogeneous $TiCl_4.THF$ and $TiCl_4.THF$ modified with $MtCl_2.THF$ (Mt = Mg or Co) catalyst systems in toluene showed a very high activity for ethylene polymerization. The catalytic systems were also capable of catalysing propylene polymerization to produce polypropylene.

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