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(54) Controlled distribution of active sites in Ziegler-Natta catalysts systems

(57) The present invention provides a method for improving and controlling the activity of Ziegler-Natta catalyst systems.

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Description

[0001] This invention relates to an improved method for activating Ziegler-Natta catalyst systems and for controlling their behaviour.

[0002] Ziegler-Natta catalyst systems are multi-site catalyst systems that typically produce polymers having a mixture of chains having different tacticities, an heterogeneous composition and properties linked to crystallisation that are not optimal. A large effort was spent to improve the activity and tacticity of these catalyst systems. The last generations of Ziegler-Natta catalyst system have an excellent productivity and the addition of a Lewis base allows the selection of isospecific sites having a high isotactic index, but they still leave a diversity of sites, both in stereospecificity and in kinetic parameters.

[0003] Metallocene and post-metallocene catalyst system on the contrary are single site catalyst systems that produce often a narrow composition distribution and uniform crystallisation but these catalysts systems are costly and difficult to prepare.

[0004] In today's polymer production, the $MgCl_2/TiCl_4$ catalyst system is largely used to prepare polyethylene and polypropylene leaving a very limited part to metallocene catalyst systems.

[0005] Conventional Ziegler-Natta catalyst systems are typically based on $MgCl_2$, $TiCl_4$ and internal Lewis base or their precursors and they are activated with AlR_3 and eventually an external Lewis base.

[0006] It is thus very desirable to prepare Ziegler-Natta catalyst systems that offer some of the advantages of single site catalyst systems but are easier and less costly to prepare than the currently available single site systems.

[0007] It is an aim of the present invention to provide a method for activating Ziegler-Natta catalyst systems.

[0008] It is also an aim of the present invention to prepare modified Ziegler-Natta catalyst system having a controlled behaviour.

[0009] It is another aim of the present invention to produce modified Ziegler-Natta catalyst systems that have and keep a good activity.

[0010] It is yet another aim of the present invention to prepare modified Ziegler-Natta catalyst system for preparing polypropylene having a good tacticity.

[0011] The present invention reaches, at least partially, one or more of these aims.

[0012] Accordingly, the present invention provides a method for either improving the activity of a finished and active Ziegler-Natta catalyst system or for activating a Ziegler-Natta pre-catalyst component by adding a Lewis acid that is a metal compound soluble in apolar solvents.

[0013] In a preferred embodiment, the present invention provides a method for activating a Ziegler-Natta pre-catalyst component that comprises the steps of:

a) providing a Ziegler-Natta pre-catalyst component;
b) optionally extracting a fraction of the titanium sites by thermal treatment for instance under vacuum;
c) treating the pre-catalyst by adding a Lewis acid BX_3 that is a boron compound soluble in apolar or polar solvents, preferably in apolar solvents, wherein X is halogen or alkyl group;
d) optionally further treating the Ziegler-Natta pre-catalyst component with a titanium compound TiX_4 before or after step c);
e) adding aluminium alkyl of general formula AlR_nZ_{3-n} wherein R is alkyl group having from 1 to 10 carbon atoms, Z is halogen and n is 0, 1, 2 or 3;

optionally adding an external electron donor $SiR^a_m(OR^b)_{4-m}$ wherein R^a and R^b are each independently selected from alkyl, aryl, cycloalkyl, arylalkyl or alkylaryl having at most 12 carbon atoms, and two neighbouring R's can be linked together to make a ring, and m is 0 or an integer from 1 to 4 .

[0014] Preferably X is Cl, Br, F or C_2H_5, more preferably it is Cl.

[0015] New internal Lewis bases such as gamma-diethers can also be used as external Lewis base. They are represented by general formula

$$R'O\text{-}(CH2 - CR^1R^2 - CH2)\text{-}OR'$$

wherein each R', R^1 and R^2 are each independently selected from alkyl, aryl, cycloalkyl, arylalkyl or alkylaryl having at most 12 carbon atoms and R^1 and R^2 can be linked together to make a ring or rings. Preferably both R' are the same and are CH3. Among preferred R^1 and R^2 one can cite isobutyl or cyclopentyl. Preferred gamma-diether is fluorenyl-based diether.

[0016] The further optional pre-catalyst treatment with TiX_4 always brings a further improvement of activity but the main improvement is caused by the addition of BX_3.

[0017] In another, less preferred embodiment, the present invention provides a method for improving the activity of

Ziegler-Natta catalyst systems that comprises the steps of;

a) providing an active Ziegler-Natta catalyst system;
b) adding a Lewis acid AX_v that is a metal compound soluble in apolar solvents,
wherein A is selected from group 13, 14 or 15 of the Periodic Table and
wherein X is halogen or alkyl group and v is the valence of A.

[0018] The method according to the present invention results in a substantial increase in the activity of the catalyst system as measured in amount of polymer produced per gram of catalyst system but in an even larger improvement of the activity as measured in amount of polymer produced per mole of titanium.

[0019] The addition of BX_3 to the Ziegler-Natta pre-catalyst has no adverse consequences on the polymers' properties.

List of figures.

[0020]

Figure 1 represents the productivity of the modified Ziegler-Natta catalyst system of the present invention expressed in g of polymer per g of catalyst per 90 min and the tacticity expressed in % as a function of the amount of added Lewis acid expressed by the molar ratio A/Mg.

Figure 2 represents the productivity, expressed in g of propylene homopolymer per g of catalyst per 90 minutes, respectively for an unmodified reference Ziegler-Natta (ZN) catalyst system, for the same ZN catalyst system thermally treated at a temperature of 120 °C, for the thermally treated ZN catalyst further treated with BCl_3 at a temperature of 90 °C and for the thermally treated ZN catalyst further treated with $TiCl_4$ at a temperature of 90 °C.

[0021] The optional thermal treatment is carried out either under vacuum or under inert gas such as helium, argon or nitrogen, at a temperature larger than 80 °C, typically of from 80 to 150 °C, preferably at a temperature of about 120 °C. It is carried out under good vacuum, preferably of the order of 10^{-10} bars and for a period of time of from 2 to 6 hours, preferably of about 4 hours. Such treatment removes a fraction of the titanium sites; it does not remove the internal base and thus does not lead to any degradation of the catalyst component up to temperatures of 150 °C under good vacuum.

[0022] A Lewis acid may act as poison, when added either simultaneously with or after the activating agent, during the preparation of an active Ziegler-Natta catalyst system. It can also act as poison when used during polymerisation. Surprisingly, in the present invention, it acts as activator of the remaining titanium sites when added prior to the activating agent.

[0023] The Lewis acid BX_3 is a halogenated or alkylated boron compound that is soluble in apolar solvents, does not interfere with the internal Lewis base used to prepare the pre-catalyst, and is colourless. The most preferred Lewis acid is BCl_3. The size of and the oxidation state of metal B play a role on the distribution and activation of the active sites: several other metals have been tested such as Si and Sn but B had by far the best performance as activator. Similarly, other halogens or alkyl groups have been tested for X, but chlorine gives the best results: the activities obtained with various X can be ranked as follows: Cl>Br>F>Ethyl.

[0024] Optionally a double pre-treatment can be carried out with TiX_4 and BX_3 before adding the aluminium alkyl activating agent: it results in a further improvement of activity.

[0025] Preferably, the pre-catalyst is treated with both BCl_3 and $TiCl_4$, added in any order, and with a molar ratio of (additional Ti)/(Ti Z-N precatalyst) of less than 1.

[0026] For example, treatment of the Ziegler-Natta pre-catalyst with BCl_3 improves the activity of the finished catalyst system by a factor of at least 2 with respect to the same untreated catalyst system. Treatment of the Ziegler-Natta pre-catalyst with BCl_3 and $TiCl_4$ improves the activity of the finished catalyst system by a factor of at least 3 with respect to the same untreated catalyst system.

[0027] Without wishing to be bound by a theory, it is believed that the Ziegler-Natta pre-catalyst consists of a combination of active titanium sites and of activating titanium sites. The thermal treatment removes part of the activating titanium sites. The subsequent Lewis acid treatment fills the vacated titanium sites with improved boron activating sites. It is also believed that the active titanium sites are not isolated but are found in aggregates of at least two titanium sites, wherein some active titanium sites may also be replaced by boron sites.

[0028] The finished pre-catalyst component is prepared according to methods well known in the art such as described for example in EP-728769 or WO03/076480 for diether-based catalysts or in US2003/0060581 for succinate- or phthalate-based catalysts. Typically, the amount of titanium in the finished pre-catalyst component is of from 1 to 4 wt%, preferably it is of the order of 2 wt%.

[0029] The Lewis acid BX_3 is preferably diluted in a convenient solvent and added to the pre-catalyst The compound is then heated from the starting temperature to a temperature of from 10 to 120 °C, preferably to a temperature of from

20 to 100 °C, more preferably to a temperature of about 90 °C and for a period of time of from 5 minutes to 4 hours, preferably 10 minutes to 2 hours. It is then dried at room temperature for a period of time of from 30 minutes to 3 hours, preferably of about 1 hour.

[0030] If the treatment with Lewis acid BX_3 is carried out for a long period of time of typically about 2 hours and at high temperature, typically of about 90 °C, all types of Ziegler-Natta pre-catalysts show an improved activity in polymerisation.

[0031] If the treatment with Lewis acid BX_3 is carried out for a short period of time of from 10 to 30 minutes and at mild temperature of from 20 to 40 °C, the Ziegler-Natta pre-catalysts prepared with phthalate internal Lewis base or with succinate internal Lewis base show improved activity when treated with BX_3 alone whereas those prepared with di-ether internal Lewis base do not show any improvement in activity when treated with BX_3 alone but have an improved activity when treated successively with TiX_4 and then with BX_3.

[0032] The amount of added Lewis acid BX_3 is preferably selected to have B/Mg ratio of less than 30. More preferably the ratio B/Mg is less than 5, most preferably it is less than 1. At such small levels of added Lewis acid, the activity is significantly increased and remains very high as a function of time. Larger amounts of Lewis acid produce a very high activity at the beginning of the polymerisation reaction followed rapidly by a sharp decrease of activity. Alternatively, the amount of Lewis acid can be given as a B/Ti ratio, but the amount of titanium is more variable as the thermal treatment removes titanium.

[0033] The temperature at which the treatment is carried out plays an important role in the productivity of the finished catalyst system: the higher the temperature, the higher the catalyst productivity.

[0034] The length of the treatment plays no significant role and the treatment can thus be limited to at most 2 hours without adverse consequences.

[0035] The productivity of the treated catalyst increases with decreasing concentration of Lewis acid $[BX_3]$ at constant value of theratio B/Mg. It is thus preferred to work at concentration of BX_3 in the suspension of at most 0.1 mol/L, more preferably of at most 0.018 mol/L, and most preferably of about 0.001 mol/L.

[0036] The monomer pressure has a positive influence on the catalyst's productivity: the higher the pressure, the higher the productivity.

[0037] The present invention also discloses the active modified Ziegler-Natta catalyst system obtained by the method described hereabove.

[0038] The activating agent and external donor are those that are typically used with conventional Ziegler-Natta catalysts. The activating agent of formula AlR_nZ_{3-n} is preferably aluminium alkyl, more preferably triethyl aluminium (TEA). The external electron donor is alkoxy-silane $SiR^a{}_m(OR^b)_{4-m}$, a more preferred being dicyclopentyldimethoxysilane (DCPDMS) or gamma-diether $R'O-(CH2 - CR^1R^2 - CH2)-OR'$, a preferred gamma-diether being fluorenyl diether (BMMF).

[0039] The present invention further discloses a method for homo- or co-polymerising ethylene or alpha olefins that comprises the steps of:

a) injecting the active modified Ziegler-Natta catalyst system into the reactor;
b) injecting monomer and optional comonomer into the reactor;
c) maintaining under polymerisation conditions;
d) retrieving a polymer.

[0040] The polymerisation results show a spectacular improvement in activity without reducing the properties of the polymers. Maximum activity is observed for low B/Mg ratio. For example, excellent results are obtained for a B/Mg ratio of about 0.02 as seen in Figure 1. It is thus important to note that in the present invention very little amount of boron is necessary to produce a very high activity. This is to be compared with the amount of aluminium, typically 100 fold larger, that is necessary to activate the catalyst.

[0041] The tacticity is also displayed in Figure 1. It increases with increasing amounts of Lewis acid for small amounts of added acid corresponding to B/Mg ratio of up to about 0.01. Further addition of Lewis acid leads to a limited decrease of tacticity.

[0042] The preferred monomer is propylene and the preferred comonomers that can be used with the modified Ziegler-Natta catalyst system of the present invention, in the copolymerisation of propylene, are ethylene and hexene.

[0043] When ethylene is used as monomer, it is observed that much improved results are obtained with a Ziegler-Natta precatalyst that contain very small amounts of titanium, typically of from 0.1 to 0.3 wt%, based on the weight of the pre-catalyst component. Additional improvements are obtained if the pre-catalyst does not contain an internal Lewis base and if the activated $MgCl_2.xTHF$ support is dried under secondary vacuum in order to extract as much as possible of tetrahydrofuran (THF). The ratio BX_3/Ti is preferably of the order of from 20 to 50. A ratio BX_3/Ti larger than 50 leads to very high initial activities, followed by steep decrease.

Examples.

Example 1- Propylene polymerisation.

[0044] A commercial Ziegler-Natta pre-catalyst prepared with a phthalate internal Lewis base was used as starting material.

[0045] The pre-catalyst underwent a thermal treatment under vacuum at a temperature of 120 °C and for a period of time of 4 hours that removed 35 % of titanium. It was then treated with BCl_3 at a temperature of 90 °C, for a period of time of 2 hours and with a B/Ti ratio of 30. This treatment removed an additional 20 % of surface titanium. For comparison, to the same thermally treated material $TiCl_4$ was added instead of BCl_3 under the same conditions.

[0046] The starting catalyst (reference), the thermally treated catalyst, the BCl_3-treated catalyst and the $TiCl_4$-treated catalyst were all used in the polymerisation of propylene under the same conditions:

- heptane: 500 mL
- polymerisation temperature = 70 °C
- propylene pressure = 4 bars added to maintain a constant pressure of 4 bars during the time of reaction
- hydrogen pressure = 0.1 bar
- cocatalyst = TEA (3 mmol/L)
- Al/Ti = 250
- external electron donor = DCPDMS (0.3 mmol/L)

[0047] The results are displayed in Figure 2 that shows

- that the productivity decreases substantially when the number of titanium sites is decreased by thermal treatment
- that it increases dramatically when further treated with BCl_3
- that not much happens when it is further treated with $TiCl_4$ instead of BCl_3.

[0048] The polypropylene obtained according to the present invention had a weight average molecular weight of the order of 350000 g/mol, a molecular weight distribution between 6.5 and 7, a melting temperature Tm of about 164 °C and an isotactic index (I.I.) of about 97 %.

[0049] In this work, the molecular weights are determined by gel permeation chromatography (GPC), the molecular weight distribution is defined by the polydispersity index that is the ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn, the melting temperature Tm is determined by DSC calorimetry as measured at the peak of fusion and the isotactic index (I.I.) is the fraction of the total polymer produced insoluble in boiling heptane.

Example 2.

[0050] The same polymerisation procedure as that described in example 1 was carried out, but the amount of BCl_3 was varied and the starting untreated pre-catalyst underwent thermal treatment. The results are summarised in Table I: they first show an increase in productivity with increasing amounts of BCl_3 followed by a plateau for values of the ratio BCl_3/Ti larger than 1.

TABLE I.

BCl_3/Ti	Prod. g/g/90min	I.I. %	Tm °C	Mn g/mol	Mw g/mol	Mw/Mn
0	1420	96.5	164.2	52500	302300	5.8
0.10	5600	98.5	163.7	49500	316600	6.4
1.0	13100	98.1	162.8	40300	293300	7.3
5.0	12730	96.8	162.4	37000	292000	7.9
31.0	12620	96.8	163	50200	313400	6.2

Example 3 - Ethylene polymerisation.

[0051] The same pre-catalyst component, the same thermal treatment and the same BCl_3 treatment conditions as those of example 1 were used. The polymerisation conditions were as follows:

Heptane : 500 mL
Cocatalyst (TEA) : 3 mmol/L
Al/Ti = 250
Ethylene pressure : 6 bars
Hydrogen pressure : 2 bars
Temperature : 80 °C

[0052] The amount of BCl_3 was varied as indicated in Table II and the starting untreated pre-catalyst underwent thermal treatment. The results are also displayed in Table II.

TABLE II.

BCl_3/Ti	Prod. g/g/90min	Tm °C	Mn g/mol	Mw g/mol	Mw/Mn
0	2920	134.0	25700	165600	6.4
0.1	3910	133.7	26000	104100	4.0
1.0	4580	133.9	25000	106100	4.2
5.0	4510	134.9	16100	97000	6.0

Example 4 - Copolymerisation of ethylene and hexene.

[0053] The same pre-catalyst component, the same thermal treatment and the same BCl_3 treatment conditions as those of example 1 were used. The polymerisation conditions were as follows:

Heptane : 300 mL
Cocatalyseur (TEA) : 3 mmol/L
Al/Ti = 250
Ethylene pressure : 4 bars
Hydrogen pressure : 1 bar
1-hexene : 80 mol% in the feed
temperature : 80 °C

[0054] The amount of BCl_3 used in the pre-catalyst was varied as displayed in Table III and the copolymerisation results are also displayed in Table III.

TABLE III.

B/Ti	B/Mg	Prod. g/g/90min	Tm °C	Mn g/mol	Mw g/mol	Mw/Mn
0	0	2580	127.6	24100	132200	5.5
0.2	0.008	6320	128.8	19100	81900	4.3
0.61	0.021	13480	130.0	24000	107900	4.5
0.91	0.03	8490	128.5	17700	91500	5.2

Example 5.

[0055] In this example, the same BCl_3 treatment was applied to pre-catalysts prepared with different internal Lewis bases (ILB). The treatment was as described in example 1 with a BCl_3/Ti ratio of 31. They were used to polymerise propylene using the polymerisation conditions of example 1.Their performances are compared in Table IV.

TABLE IV.

ILB	BCl_3/Ti	Prod. g/g/90min	I.I. %	Tm °C	Mw kg/mol	Mw/Mn
Phthalate	0	5420	98.8	163.2	316	7.2

(continued)

ILB	BCl_3/Ti	Prod. g/g/90min	I.I. %	Tm °C	Mw kg/mol	Mw/Mn
Succinate	0	4390	98.2	162.5	307.6	9.4
γ-diether*	0	8200	93.6	162.4	202.5	5.5
Phthalate	31	11950	97.5	162.7	340.13	7.7
Succinate	31	14180	96.9	162.4	352.5	9.9
γ-diether	31	12460	89.3	160.7	215.9	5.2
* : no external Lewis base was used in this example.						

Example 6.

[0056] In this example, the 3 pre-catalysts of example 5 were treated with increasing amounts of BCl_3, all other conditions being unchanged. The results are displayed in Table V.

TABLE V

BCl_3/Ti	Prod. g/g/90min	I.I. %	Tm °C	Mw kg/mol	Mw/Mn
phthalate					
0	8370	98.4	163.2	324.2	7.1
0.1	9960	97.9	162.8	335.1	7.2
0.25	10890	97.7	164.6	333.3	7.7
0.5	10970	97.0	163.5	344	8.2
1.0	10200	97.5	162.9	327.9	6.2
5.0	9780	98.0	163.1	338.4	7.7
31.0	11950	97.5	162.7	340.1	7.7
succinate					
0	10980	97.4	163.0	365	8.3
0.5	13250	96.8	162.5	376.3	8.6
1.0	14790	97.2	162.9	351.2	8.4
2.0	12320	97.3	163.8	311.7	7.5
31.0	14180	96.9	162.4	352.5	9.9
γ-diether					
0	7830	94.3	162.0	253.7	4.0
0.25	12160	93.7	160.6	158.4	3.5
0.5	13220	90.9	160.0	188.1	3.6
0.75	13250	91.8	160.7	206.7	4.1
1.0	10760	91.5	160.4	192.5	3.5
2.0	10420	88.9	161.4	200	4.4
31.0	12460	89.3	160.7	215.9	5.2

[0057] It can be concluded that all types of pre-catalysts show that at first the productivity increases with increasing amount of BCl3, it reaches a maximum and then decreases slowly. The position of the maximum varies with the nature of the pre-catalyst.

Example 7.

[0058] The polymerisation procedure of example 1 was repeated with the exception that the BCl_3 treatment temperature was varied. The results are reported in Table VI.

TABLE VI.

Treatment Temperature °C	Production g/g/90min	I.I. %	Tm °C	Mw kg/mol	Mw/Mn
None	7550	98.0	164.1	318.2	7.5
20	11660	98.0	164.9	327.2	6.5
40	14740	97.7	162.8	245	5.3
60	15020	97.4	164.3	299.3	5.5
90	16250	97.9	162.1	316.6	6.4
Heptane reflux	16340	98.7	161.1	265.4	5.1

[0059] It can thus be concluded that the productivity of the catalyst initially increases rapidly with increasing treatment temperature up to a treatment temperature of about 60 °C. For temperatures higher than 60 °C it keeps increasing but at a very slow rate.

Example 8.

[0060] The polymerisation procedure of example 1 was repeated except that the concentration in BCl_3 was varied while maintaining a constant B/Ti ratio. The results are displayed in Table VII.

TABLE VII.

[BCl_3] mol/L	Productivity g/g/90min	I.I. %	Tm °C	Mw kg/mol	Mw/Mn
0.001	16800	97.0	162.5	337.1	5.7
0.018	16250	97.9	162.1	316.6	6.4
0.1	14140	97.4	161.9	266.7	5.7

[0061] The results show that the productivity increases with decreasing concentration in BCl_3.

[0062] The polymerisation procedure of example 1 was repeated except that the propylene pressure was varied. The results are displayed in Table VIII.

TABLE VIII.

Propylene pressure bars	Production g/g/90min	I.I. %	Tm °C	Mw kg/mol	Mw/Mn
4	16250	97.9	162.1	316.6	6.4
8	29100	97.8	163.1	385	5.3

[0063] As expected, the catalysts's productivity increases with increasing propylene pressure.

Example 9.

[0064] In this example, treatment of a phthalate-based pre-catalyst with BCl_3 was carried out under very mild conditions with a B/Ti ratio of 0.5. The activation and polymerization procedures was the same as in the other examples. The treatment conditions and polymerisation results are reported in Table IX.

TABLE IX.

Time min	Temp. °C	Production g/g/90min	I.I. %	Tm °C	Mw kg/mol	Mw/Mn
-	-	7550	98.0	164.1	318.2	7.5

(continued)

Time min	Temp. °C	Production g/g/90min	I.I. %	Tm °C	Mw kg/mol	Mw/Mn
10	20	12810	98.1	163.7	267.2	6.2
30	40	14390	98.3	163.3	253.7	6.2

[0065] These results confirm that the productivity increases with increasing temperature of the BCl_3 treatment. The duration of treatment is not very relevant.

Example 10.

[0066] Several types of Ziegler-Natta pre-catalysts were submitted to mild treatment conditions: the pre-catalysts were not submitted to thermal treatment and were treated with BCl3 during 10 minutes at a temperature of 70 °C. They were then used to polymerize propylene under the following conditions:

500 mL of heptane
[TEA] : 3 mmol/L
[DCPDMS] : 0.3 mmol/L
Al/Ti = 250 for phthalate- and succinate-based pre-catalyst and = 160 for γ-diether-based pre-catalyst
Propylene pressure = 4 bars
Polymerisation temperature = 70 °C
Volume H_2 = 57 cm^3 for phthalate- and succinate-based pre-catalyst and = 14 cm^3 for γ-diether-based pre-catalyst.

[0067] The results are reported in Table X.

TABLE X.

Pre-catalyst	B/Ti	Productivity g/g/90min	I.I. %	Tm °C	Mw kg/mol	Mw/Mn
phthalate	-	7550	98.0	164.1	318.2	7.5
succinate	-	4390	98.2	162.5	307.6	9.4
diether	-	8200	93.6	162.4	202.5	5.5
phthalate	0.5	12220	98.3	162.2	295.2	6.0
succinate	0.5	12220	98.2	162.3	310.6	9.4
diether	0.5	6400	92.8	160.8	211.2	4.5

[0068] With this type of treatment, it can be seen that the succinate-based pre-catalysts respond best to the treatment based.

[0069] The behaviour of the diether-based pre-catalysts was considerably improved when they were treated with $TiCl_4$ prior to the BCl_3 treatment as can be seen in Table XI.

TABLE XI.

Prior Treatment with $TiCl_4$	Productivity g/g/90min	I.I. %	Tm °C	Mw kg/mol	Mw/Mn
$(Ti_{add})/(Ti_{cata})$ =0	6400	92.8	160.8	211.2	4.5
$(Ti_{add})/(Ti_{cata})$ = 0.25	8200	92.4	164.1	202.7	4.1
$(Ti_{add})/(Ti_{cata})$ = 0.5	8400	95.7	163.9	193.4	3.9

Example 11.

[0070] In this example, the pre-catalyst has been treated sequentially with two different Lewis acids. The pre-catalysts were first treated with BCl_3 and then with $TiCl_4$. In all the cases studied, the addition of a further Lewis acid always produced an increase in productivity, but the main increase was always produced by the addition of BCl_3.

[0071] The phthalate-based pre-catalyst had an initial productivity of 7550 grams of polypropylene per gram of catalyst per 90 minutes. When treated first with BCl_3 (B/Ti = 0.5) alone, the productivity was increased to 16250 grams of polypropylene per gram of catalyst per 90 minutes. When treated with $TiCl_4$ (Ti/Ti = 0.5) alone, the productivity was of 8960 grams of polypropylene per gram of catalyst per 90 minutes.

[0072] When treated first with BCl_3(B/Ti = 0.5) and next with $TiCl_4$ (Ti/Ti = 0.5), the productivity increased to 23600 grams of polypropylene per gram of catalyst per 90 minutes. Double treatment thus leads to the highest productivity.

Claims

1. A method for activating a Ziegler-Natta pre-catalyst component that comprises the steps of:

a) providing a Ziegler-Natta pre-catalyst component;
b) optionally submitting the pre-catalyst to a thermal treatment;
c) treating the pre-catalyst by adding a Lewis acid BX_3 that is a boron compound soluble in apolar solvents, wherein X is halogen or alkyl group;
d) optionally further treating the Ziegler-Natta pre-catalyst component with a titanium compound TiX_4 before or after step c);
e) adding aluminium compound of general formula AlR_nZ_{3-n} wherein R is alkyl group having from 1 to 10 carbon atoms, Z is halogen and n is 0, 1, 2 or 3;
f) optionally adding an external electron donor either of general formula $SiR^a_m(OR^b)_{4-m}$ or of general formula R'O-(CH2 - CR^1R^2 - CH2)-OR' wherein R^a and R^b are each independently selected from alkyl, aryl, cycloalkyl, arylalkyl or alkylaryl having at most 12 carbon atoms, and two neighbouring R can be linked together to make a ring, m is 0 or an integer from 1 to 4, wherein each R', R^1 and R^2 is independently selected from alkyl, aryl, cycloalkyl, arylalkyl or alkylaryl having at most 12 carbon atoms, and R^1 and R^2 can be linked together to make a ring or rings.

2. The method of claim 1 wherein X is Cl, Br, F or C_2H_5.

3. The method of claim 2 wherein X is Cl.

4. The method of any one of claims 1 to 3 wherein the thermal treatment is carried out at a temperature of from 80 to 150 °C under vacuum better than 10^{-5} bars.

5. The method of any one of the preceding claims wherein wherein the aluminium compound is an aluminium alkyl.

6. The method of any one of the preceding claims wherein the molar ratio B/Mg is of at most 30.

7. The method of claim 6 wherein the molar ratio B/Mg is of less than 1.

8. The method of any one of the preceding claims wherein further comprising the additional treatment with TiX_4 wherein X is halogen, preferably Cl.

9. The method of claim 8 wherein the molar ratio of (additional Ti)/(Ti ZN precatalyst) is of less than 1.

10. A modified active Ziegler-Natta catalyst system obtainable by the method of any one of claims 1 to 9.

11. A method for homo- or co-polymerising propylene that comprises the steps of:

a) injecting the active modified Ziegler-Natta catalyst system of claim 10 into the reactor;
b) injecting the monomer and optional comonomer into the reactor;
c) maintaining under polymerisation conditions;
d) retrieving a polymer.

12. The method of claim 11 wherein the monomer is propylene or ethylene and the optional comonomer is ethylene, propylene or 1-hexene.

FIGURE 1

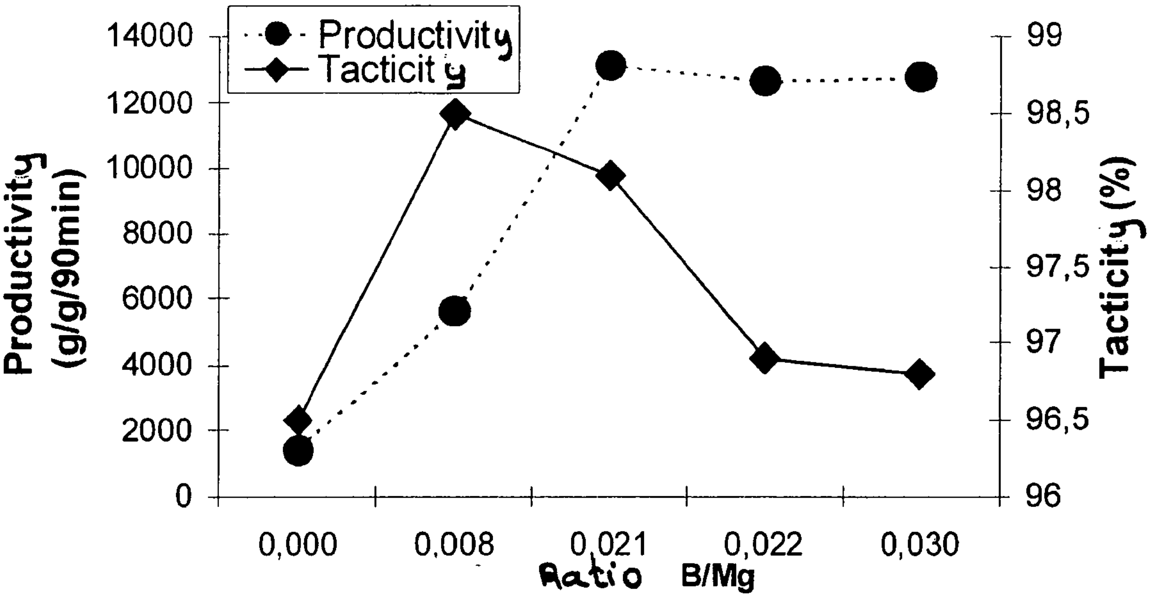
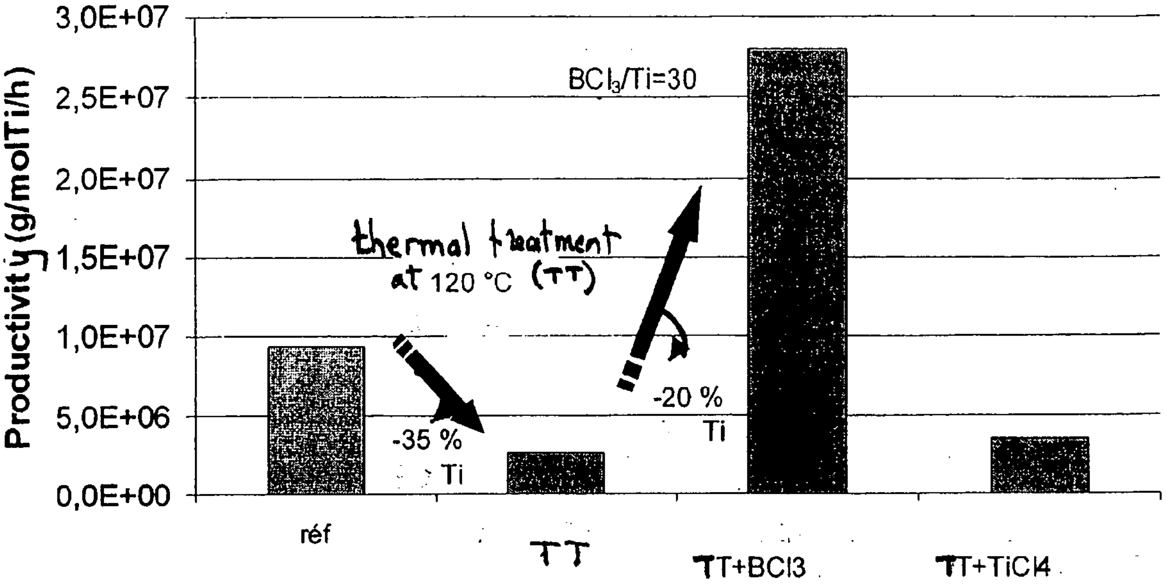

Productivity
Tacticity
14000
12000
10000
8000
6000
4000
2000
0
Productivity (g/g/90min)
99
98,5
98
97,5
97
96,5
96
Tacticity (%)
0,000
0,008
0,021
0,022
0,030
Ratio B/Mg

FIGURE 2


Productivity (g/molTi/h)
3,0E+07
2,5E+07
2,0E+07
1,5E+07
1,0E+07
5,0E+06
0,0E+00
BCl3/Ti=30
thermal treatment at 120 °C (TT)
-35 % Ti
-20 % Ti
réf
TT
TT+BCl3
TT+TiCl4

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EUROPEAN SEARCH REPORT

Application Number
EP 06 29 0629

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	7 September 2006	BALMER, J

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