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(54) Title: INDAZOLE-MODIFIED ZIEGLER-NATTA CATALYST SYSTEM

(57) Abstract: A modified Ziegler-Natta catalyst system, a method for preparing the catalyst system, and a process for polymerizing an olefin in the presence of the catalyst system are disclosed. The catalyst system comprises a titanium or vanadium compound, an aluminum compound, and an indazole. Improved comonomer incorporation and the ability to regulate molecular weight are achieved in the manufacture of polyolefins.



88-2217A

INDAZOLE-MODIFIED ZIEGLER-NATTA CATALYST SYSTEM**FIELD OF THE INVENTION**

5 This invention relates to a modified Ziegler-Natta catalyst system. The catalyst system includes an indazole which influences polyolefin properties such as comonomer incorporation.

BACKGROUND OF THE INVENTION

10 Interest in catalysis continues to grow in the polyolefin industry. Many olefin polymerization catalysts are known, including conventional Ziegler-Natta catalysts. To improve polymer properties, single-site catalysts, in particular metallocenes are beginning to replace Ziegler-Natta catalysts. Single-site catalysts typically require large amounts of expensive activators such as methylalumoxane or salts of non-
15 nucleophilic anions such as triphenylcarbenium tetrakis(pentafluorophenyl)borate. It would be desirable to incorporate some of the advantages of single-site catalysts, such as good comonomer incorporation, without the high cost due to the activators.

 Ziegler-Natta catalyst systems are well known in the art. Useful Ziegler-Natta catalysts include titanium or vanadium compounds and their combinations with
20 aluminum compounds. In some circumstances, mixtures are preferred (U.S. Pat. Nos. 3,218,266, 4,483,938, 4,739,022, and 5,492,876 use mixtures of vanadium and titanium-based Ziegler-Natta catalysts), but commonly a single titanium or vanadium compound is used. It is known to support the titanium or vanadium compound with compounds such as silica or magnesium chloride and considerable research has
25 been done in this area. Known compositions also include an aluminum compound, sometimes referred to as a cocatalyst. Trialkyl aluminums, dialkyl aluminum halides, and alkyl aluminum dihalides are common cocatalysts.

 It is known to add other compounds to a Ziegler-Natta catalyst system to influence catalytic properties. Various Lewis bases have been used; they are often
30 referred to as modifiers or electron donors. When the electron donor is added during the preparation of the Ziegler-Natta catalyst system it is sometimes called an "internal donor," while those added during or immediately prior to the polymerization have been called "external donors." A variety of electron donors have been

disclosed (for example, see U.S. Pat. No. 4,136,243). Common electron donors include ethers and esters (for example, see U.S. Pat. No. 5,968,865), but many others have been used. U.S. Pat. No. 5,106,926 gives examples of suitable electron donors as alkyl esters of aliphatic or aromatic carboxylic acids, aliphatic ketones, aliphatic amines, aliphatic alcohols, alkyl or cycloalkyl ethers, and mixtures thereof with tetrahydrofuran being preferred. U.S. Pat. No. 4,927,797 discloses the use of silane donors such as methylcyclohexyldimethoxysilane, and U.S. Pat. No. 6,228,792 discloses the use of 2,6-disubstituted pyridines as electron donors. Sometimes two or more electron donors are used. U.S. Pat. No. 7,560,521 teaches a combination of a monofunctional donor selected from ethers, esters, amines, or ketones with a difunctional donor selected from diesters, diketones, diamines, or diethers. U.S. Pat. No. 6,436,864 discloses unsaturated nitrogenous compounds as electron donors. An imine, a diimine, and a methoxymethylpyridine are used in the examples. Indazoles are not disclosed.

The role of donors is not completely understood and remains a subject of continued research. As polyolefin applications become more demanding, there is a continued need for improvements in catalyst systems. Despite the considerable research that has been done in this area, apparently no one has studied indazoles as a component of a Ziegler-Natta catalyst system.

SUMMARY OF THE INVENTION

In one aspect, the invention is a modified Ziegler-Natta catalyst system and a method for preparing it. In another aspect, the invention is a process for polymerizing an olefin in the presence of the catalyst system. The catalyst system, which comprises a titanium or vanadium compound, an aluminum compound, and an indazole, enables improved comonomer incorporation and molecular weight regulation in the manufacture of polyolefins.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a modified Ziegler-Natta catalyst system comprising: (a) a titanium or vanadium compound; (b) an aluminum compound selected from the group consisting of trialkyl aluminums, dialkyl aluminum halides, alkyl aluminum dihalides, and combinations thereof; and (c) an indazole. The titanium or vanadium compound can be any compound normally effective as a Ziegler-Natta catalyst.

Preferred titanium compounds include titanium halides such as titanium trichloride and titanium tetrachloride, and titanium alkoxides such as titanium(IV) butoxide. Preferred vanadium compounds include vanadium halides such as vanadium tetrachloride, vanadium oxyhalides such as vanadium oxytrichloride, and vanadium
5 alkoxides such as vanadium(V) oxytriethoxide. Mixtures of titanium compounds and vanadium compounds may be used.

More preferably, titanium tetrachloride is used. When titanium tetrachloride is used, it is preferably supported on or modified with a magnesium compound. Many magnesium compounds suitable for use in supporting or modifying the Ziegler-Natta
10 catalysts are well known. Examples include magnesium chloride, alkyl magnesium halides, and magnesium siloxanes. For additional examples, see U.S. Pat. Nos. 4,298,718, 4,399,054, 4,495,338, 4,464,518, 4,481,301, 4,518,706, 4,699,961, 5,258,345, 6,291,384, and 7,560,521, the teachings of which are incorporated herein by reference.

15 Optionally, a Lewis base is also included in the catalyst system. Preferred Lewis bases are C₃-C₂₄ esters such as butyl acetate, diethyl phthalate, trimethyl trimellitate, and diethyl adipate and C₄-C₁₆ ethers such as dibutyl ether, glyme, and diglyme. More preferred Lewis bases are C₉-C₂₄ esters such as diethyl phthalate, dioctyl isophthalate, and 1,6-hexanediol bisbenzoate.

20 In one aspect, the titanium compound is a titanium halide supported on magnesium chloride, and the Lewis base, if any, is present in a Lewis base/Ti molar ratio less than 1. The supported titanium compound preferably has as a porosity (P_F) determined with the mercury method higher than 0.3 cm³/g, and typically in the range of 0.50-0.80 cm³/g. The total porosity (P_T) is usually in the range of 0.50-1.50
25 cm³/g, preferably from 0.60-1.20 cm³/g. The surface area measured by the BET method is preferably lower than 80, more preferably from 10 to 70 m²/g. The porosity measured by the BET method is generally from 0.10 to 0.50, preferably from 0.10 to 0.40 cm³/g.

30 Particles of the magnesium chloride-supported titanium compound preferably have substantially spherical morphology. Average diameters are preferably from 5 to 150 μm, more preferably from 20 to 100 μm. "Substantially spherical" particles are those wherein the ratio between the major axis and minor axis is less than or equal to 1.5, preferably less than 1.3.

The titanium compound preferably has the formula $Ti(OR^I)_nX_{y-n}$, wherein n has a value from 0 to 0.5, y is the valence of titanium, R^I is a C_1 - C_8 alkyl, cycloalkyl or aryl radical, and X is halogen. Preferably, R^I is ethyl, isopropyl, n-butyl, isobutyl, 2-ethylhexyl, n-octyl, phenyl, or benzyl; X is preferably chlorine. $TiCl_4$ is especially preferred.

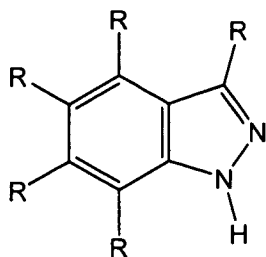
One method suitable for preparing the spherical components mentioned above comprises a first step in which a compound $MgCl_2 \cdot mR^{III}OH$, wherein $0.3 \leq m \leq 1.7$ and R^{III} is a C_1 - C_{12} alkyl, cycloalkyl or aryl radical, reacts with the titanium compound of formula $Ti(OR^I)_nX_{y-n}$.

The compounds are conveniently obtained by mixing alcohol and magnesium chloride in the presence of an inert hydrocarbon immiscible with the adduct with stirring at the melting temperature of the adduct (100 - $130^\circ C$). The emulsion is quickly quenched, and the adduct solidifies as spherical particles. Suitable methods for preparing the spherical adducts are disclosed, e.g., in U.S. Pat. Nos. 4,469,648 and 4,399,054, the teachings of which are incorporated herein by reference. Another useful method for making the spherical components is spray cooling, described, e.g., in U.S. Pat. Nos. 5,100,849 and 4,829,034.

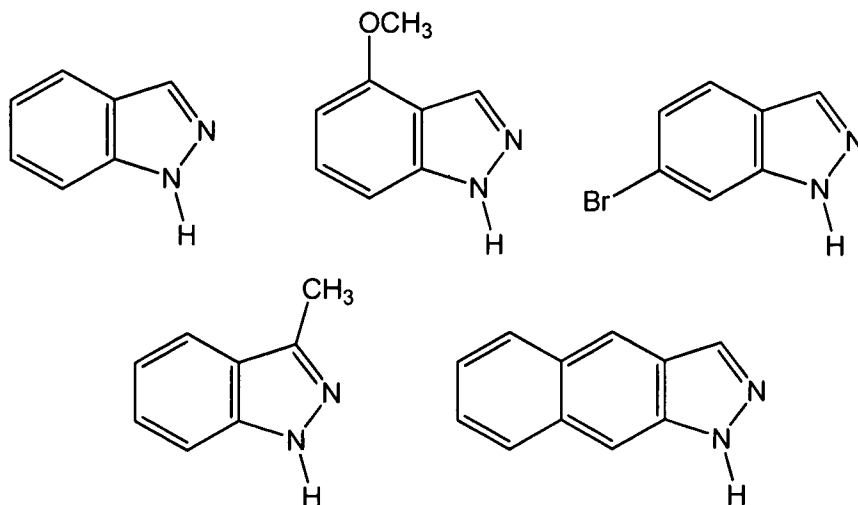
For more examples of suitable titanium compounds and their methods of preparation, see U.S. Pat. Nos. 4,399,054 and 6,627,710, the teachings of which are incorporated herein by reference.

The modified Ziegler-Natta catalyst system includes an aluminum compound selected from the group consisting of trialkyl aluminums, dialkyl aluminum halides, alkyl aluminum dihalides, and combinations thereof. Suitable aluminum compounds include triethylaluminum, tri-isobutylaluminum, diethylaluminum chloride, butylaluminum dichloride, and the like, and mixtures thereof. Trialkyl aluminum compounds are preferred. Preferably, the molar ratio of the aluminum compound to titanium compound is within the range of 0.5:1 to 500:1.

The modified Ziegler-Natta catalyst system includes an indazole. By "an indazole," we mean indazole and substituted indazoles. Preferably, the indazole has the structure:



wherein each R is independently H, Cl, Br, or C₁-C₁₆ hydrocarbonyl. Some examples of suitable indazoles are shown below:



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Indazoles can be prepared using a variety of methods known in the art. One convenient method is by treatment of the corresponding o-fluorobenzaldehyde with hydrazine. This and other methods are discussed in *J. Org. Chem.* **71** (2006) 8166. Preferably, each R is H. When each R is H, the compound is indazole. Preferably, the molar ratio of the indazole to titanium or vanadium compound is within the range of 1:1 to 50:1, more preferably from 10:1 to 30:1.

The modified Ziegler-Natta catalyst system is useful for polymerizing olefins. Preferably, the olefin is an α -olefin. Preferred α -olefins are ethylene, propylene, 1-butene, 1-hexene, 1-octene, and mixtures thereof. More preferred are ethylene, propylene, and combinations of ethylene with propylene, 1-butene, 1-hexene, or 1-octene. When ethylene is polymerized in combination with another α -olefin, the modified Ziegler-Natta catalyst system produces polyethylene with good incorporation of the α -olefin (see Example 2 and Comparative Example 3 in Table 1, below). The amount of α -olefin incorporation will depend upon the particular α -olefin and the amount added to the polymerization. The level of α -olefin incorporation can be easily measured by FT-IR spectroscopy. Each molecule of α -olefin incorporated

gives one tertiary carbon atom. As the comparative examples in Table 1 show, the positive impact on branching appears to be specific to indazoles.

The modified Ziegler-Natta catalyst system can also be used to regulate molecular weight. We found that including an indazole reduces the weight average
5 molecular weight of the polyolefin (see Example 2 and Comparative Example 3 in Table 1, below). The result is surprising because including other similar heterocyclic amines such as pyrazole, substituted pyrazoles, and benzocinnoline in the Ziegler-Natta catalyst do not reduce the M_w value of the polyolefin.

Optionally, hydrogen is used to regulate polyolefin molecular weight. The
10 addition of hydrogen effectively decreases the molecular weight. The amount of hydrogen needed depends upon the desired polyolefin molecular weight and melt flow properties. Generally, as the amount of hydrogen is increased, the polyolefin molecular weight decreases and the melt index (MI) increases. For many applications, the polyolefin melt index will be too low if the polymerization is
15 performed in the absence of hydrogen.

The polymerizations are normally conducted under pressure. The pressure is preferably in the range of 0.2 MPa to 35 MPa, more preferably from 0.4 MPa to 25 MPa.

Many types of polymerization processes can be used, including gas phase,
20 bulk, solution, or slurry processes. The polymerization can be performed over a wide temperature range. Generally, lower temperatures give higher molecular weight and longer catalyst lifetimes. However, because the polymerization is exothermic, lower temperatures are more difficult and costly to achieve. A balance must be struck between these two factors. Preferably, the temperature is within the
25 range of 0°C to 150°C. A more preferred range is from 20°C to 90°C.

Catalyst concentrations used for the olefin polymerizations depend on many factors. Preferably, however, the concentration ranges from about 0.01 micromoles titanium or vanadium compound per liter to about 100 micromoles per liter. Polymerization times depend on the type of process, the catalyst concentration, and
30 other factors. Generally, polymerizations are complete within several seconds to several hours.

The modified Ziegler-Natta catalyst system can be made by any suitable method; those skilled in the art will recognize a variety of acceptable synthetic

strategies. Each component can be separately added to the polymerization reactor. Preferably, two or more components are combined prior to addition. For example, the indazole may be reacted with the titanium or vanadium compound prior to addition to the polymerization reactor. In one preferred method, the indazole is reacted with the aluminum compound prior to addition to the reactor. More preferably, the indazole is reacted with the aluminum compound and the reaction mixture is contacted with a titanium or vanadium compound. This mixture is then added to the polymerization reactor. Most preferably, the indazole is reacted with the aluminum compound and the reaction mixture is contacted with a titanium compound that has been supported on a magnesium compound, especially magnesium chloride.

The following examples merely illustrate the invention. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

EXAMPLE 1

Modified Ziegler-Natta Catalyst System

A magnesium chloride and ethanol adduct is prepared following the method described in Example 2 of U.S. Pat. No. 4,399,054, but working at 2000 RPM instead of 10,000 RPM. The adduct is treated thermally under a nitrogen stream, over a temperature range of 50-150°C, until a weight content of 25% of ethanol is reached. In a 2-L four-neck flask, purged with nitrogen, TiCl_4 (1 L) is charged at 0°C followed by the spherical MgCl_2 /ethanol adduct (70 g). The temperature is raised to 130°C in 2 hours and maintained for 1 hour. The stirring is discontinued, the solid product is allowed to settle, and the supernatant liquid is removed by siphoning. Fresh TiCl_4 is charged to the flask, the temperature is brought to 110°C and maintained for 60 minutes. The stirring is discontinued, the solid product is allowed to settle, and the supernatant liquid is removed by siphoning. The solid residue is washed once with heptane at 80°C, five times with hexane at 25°C, dried under vacuum at 30°C, and analyzed. The resulting solid contains 3.5% by weight titanium.

Indazole (47.3 mg, 4×10^{-4} mole) is added to a solution of triethylaluminum (4×10^{-4} mole) in hexanes. The solution is stirred for 1 hour and 20 mg (2×10^{-5} mole

Ti) of titanium tetrachloride supported on magnesium chloride (prepared as described above) is added. The mixture is stirred for 30 minutes and used as described below in an olefin polymerization.

EXAMPLE 2

Polymerization

Isobutane (1 L), 1-butene (20 mL), and 1M triethylaluminum solution in hexanes (4 mL) are added to a dry, stainless-steel 2-L autoclave reactor. The reactor is heated to 80°C and hydrogen is added from a 300-mL vessel at 4.10 MPa to effect a pressure drop of 0.34 MPa. The reactor is pressurized to 0.7 MPa with ethylene. The polymerization reaction is started by injecting the modified catalyst system from Example 1. The temperature is maintained at 80°C and ethylene is supplied on demand to maintain the reactor pressure of 0.7 MPa. After 51 minutes, the polymerization is terminated by venting the autoclave. The resulting polyethylene is dried and tested.

Yield: 51 g. Activity: 2900 g polyethylene per g supported titanium compound per hour. By GPC, the polyethylene has a weight-average molecular weight (M_w) of 115,000 and a M_w/M_n of 3.2. Branching (by FT-IR spectroscopy): 17.7 tertiary carbons per 1000 carbons. Percent crystallinity (by differential scanning calorimetry): 46%. Melt index (MI) according to ASTM D-1238, Condition E: 4.8 dg/min. Rheological testing is performed, and ER, an elasticity parameter measured according to ASTM D4440-95A (and as described in U.S. Pat. Nos. 5,534,472 and 6,713,585 and in R. Shroff and H. Mavridis, J. Appl. Polym. Sci. **57** (1995) 1605), is 3.2.

COMPARATIVE EXAMPLE 3

The polymerization of Example 2 is repeated, but with a catalyst system that does not contain indazole. The system is prepared by adding 20 mg (2×10^{-5} mole Ti) of the same titanium compound to a solution of triethylaluminum (4×10^{-4} mole) in hexanes. The results are shown in Table 1.

COMPARATIVE EXAMPLE 4

The polymerization of Example 2 is repeated, but with a catalyst system that uses pyrazole (4×10^{-4} mole) as a replacement for indazole. The results are shown in Table 1.

COMPARATIVE EXAMPLE 5

The polymerization of Example 2 is repeated, but with a catalyst system that uses 3,5-dimethylpyrazole (4×10^{-4} mole) as a replacement for indazole. The results are shown in Table 1.

COMPARATIVE EXAMPLE 6

The polymerization of Example 2 is repeated, but with a catalyst system that uses 3,5-diphenylpyrazole (4×10^{-4} mole) as a replacement for indazole. The results are shown in Table 1.

COMPARATIVE EXAMPLE 7

The polymerization of Example 2 is repeated, but with a catalyst system that uses benzo[c]cinnoline (4×10^{-4} mole) as a replacement for indazole. The results are shown in Table 1.

Table 1

Ex.	Time (min)	Activity	MI	<u>Polymerizations</u>		Branches /1000 C	Crystallinity (%)	ER
				M _w	M _w /M _n			
2	51	2900	4.8	115,000	7.9	17.7	46	3.2
C3	30	8800	2.6	134,000	7.8	11.7	53	2.4
C4	46	6000	3.2	128,000	7.1	11.0	51	2.2
C5	44	8700	0.9	149,000	6.5	7.7	55	2.1
C6	79	5400	1.3	140,000	6.6	9.7	53	2.0
C7	64	2100	0.2	193,000	6.0	7.0	55	2.4

Example 2 shows that the use of an indazole provides improved comonomer incorporation. Each molecule of incorporated 1-butene provides a branch site. There are 17.7 branches per 1000 carbons with indazole versus 11.7 in the control experiment without indazole (Comparative Example 3). Inspection of Comparative Examples 4-7 shows that this is an unexpected result; other similar heterocyclic

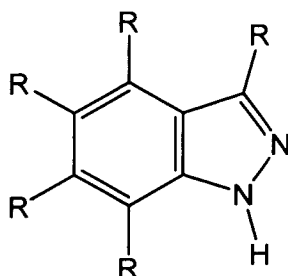
amines such as pyrazole, substituted pyrazoles, and benzocinnoline have decreased comonomer incorporation.

Example 2 also shows that the use of an indazole allows polyolefin molecular weight to be regulated. The M_w of this polymer is lower than that of the polyolefin made without indazole (Comparative Example 3). Inspection of Comparative Examples 4-7 shows that this is an unexpected result; other similar heterocyclic amines such as pyrazole, substituted pyrazoles, and benzocinnoline provide little or no reduction in M_w .

The preceding examples are meant only as illustrations. The following claims define the invention.

We claim:

1. A modified Ziegler-Natta catalyst system comprising: (a) a titanium or vanadium compound; (b) an aluminum compound selected from the group consisting of trialkyl aluminums, dialkyl aluminum halides, alkyl aluminum dihalides, and combinations thereof; and (c) an indazole.
2. The catalyst system of claim 1 wherein the titanium or vanadium compound is selected from the group consisting of titanium halides, titanium alkoxides, vanadium halides, vanadium oxyhalides, vanadium alkoxides, and combinations thereof.
3. The catalyst system of claim 1 wherein the indazole has the structure:



wherein each R is independently H, Cl, Br, or C₁-C₁₆ hydrocarbyl.

4. The catalyst system of claim 3 wherein each R is H.
5. The catalyst system of claim 1 wherein the molar ratio of indazole to titanium is from 1:1 to 50:1.
6. A process which comprises polymerizing an olefin in the presence of the catalyst system of claim 1.
7. The process of claim 6 wherein the olefin is selected from the group consisting of ethylene, propylene, 1-butene, 1-hexene, 1-octene, and combinations thereof.
8. A method for preparing a modified Ziegler-Natta catalyst system, said method comprising: (a) reacting an indazole with an aluminum compound selected from the group consisting of trialkyl aluminums, dialkyl aluminum halides, alkyl aluminum dihalides, and combinations thereof; and (b) contacting the reaction mixture from step (a) with a titanium or vanadium compound.

9. A process which comprises polymerizing an olefin in the presence of a modified Ziegler-Natta catalyst system prepared by the method of claim 8.
10. A modified Ziegler-Natta catalyst system comprising the product obtained by contacting: (a) a titanium or vanadium compound; (b) an aluminum compound selected from the group consisting of trialkyl aluminums, dialkyl aluminum halides, alkyl aluminum dihalides, and combinations thereof; and (c) an indazole.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/002639

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F10/00 C08F4/639 C08F4/631 C08F4/635
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/065816 A2 (BASELL POLIOLEFINE SRL [IT]; LIGUORI DARIO [IT]; FOCANTE FRANCESCA [IT] 14 June 2007 (2007-06-14) claims 1,2,7,10 page 3, line 10 page 6, paragraph 2 page 7, paragraph 3 page 8, paragraph 1 page 10, paragraph 4 -----	1-10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/002639

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2007065816 A2	14-06-2007	EP 1957545 A2	20-08-2008
		JP 2009518481 T	07-05-2009
		US 2009156391 A1	18-06-2009
