

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau



(10) International Publication Number

WO 2014/149628 A1

(43) International Publication Date

25 September 2014 (25.09.2014)

WIPO | PCT

(51) International Patent Classification:

C08F 4/64 (2006.01) C08F 10/00 (2006.01)
C08F 4/654 (2006.01) C08F 2/00 (2006.01)

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(21) International Application Number:

PCT/US2014/019961

(22) International Filing Date:

3 March 2014 (03.03.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13/840,182 15 March 2013 (15.03.2013) US

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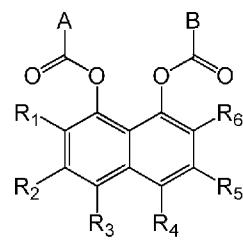
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

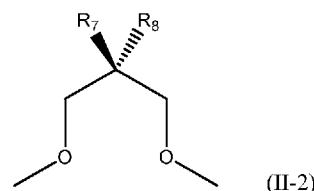
Published:

— with international search report (Art. 21(3))

(54) Title: MIXED INTERNAL DONOR STRUCTURES FOR 1-OLEFIN POLYMERIZATION CATALYSTS



(II-1)



(II-2)

(57) Abstract: Solid catalyst components are disclosed, which include titanium, magnesium, halogen and a combination of internal electron donor compounds containing at least one 1,8 naphthyl diester compound of Formula (II-1) and at least one 3,3-bis(methoxymethyl) alkane of Formula (II-2); wherein R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, A, and B are described herein. Catalyst systems containing the catalyst solid components, organoaluminum compounds, and organosilicon compounds are also discussed. This disclosure relates to methods of making the solid catalyst components and the catalyst systems, and methods of polymerizing or copolymerizing alpha olefins using the catalyst systems.

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**MIXED INTERNAL DONOR STRUCTURES FOR 1-OLEFIN
POLYMERIZATION CATALYSTS**

TECHNICAL FIELD

5 The embodiments of the present disclosure relate to solid catalyst components for olefin polymerization. In particular, the solid catalyst components comprise titanium, magnesium, halogen and a combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound. The 1,8-naphthyl diester compounds include naphthalene-1,8-diyl dicycloalkanecarboxylate 10 derivatives, and 8-(cycloalkenecarbonyloxy)naphthalene-1-yl benzoate derivatives. The embodiments of the present disclosure further relate to catalyst systems containing the solid catalyst components, methods of making the solid catalyst components and the catalyst systems, and methods of polymerizing or copolymerizing alpha-olefins using the catalyst systems.

BACKGROUND

15 Polyolefins are a class of polymers derived from simple olefins. Known methods of making polyolefins involve the use of Ziegler-Natta polymerization catalysts. These catalysts polymerize vinyl monomers using a transition metal halide to provide a polymer with an isotactic stereochemical configuration.

Basically two types of Ziegler-Natta catalyst systems are used in the normal processes for 20 the polymerization or copolymerization of olefins. The first one, in its broadest definition, comprises $TiCl_3$ based catalysts components, obtained for example by reduction of $TiCl_4$ with Al-alkyls, used in combination with Al-compounds such as diethylaluminum chloride (DEAC). Despite the modest properties of the polymers in terms of isotacticity the catalysts are

characterized by a very low activity which causes the presence of large amounts of catalytic residues in the polymers.

The second type of catalyst system comprises a solid catalyst component, constituted by a magnesium dihalide on which are supported a titanium compound and internal electron donor compound. In order to maintain the high selectivity for an isotactic polymer product, a variety of internal electron donor compounds must be added during the catalyst synthesis. Conventionally, when a higher crystallinity of the polymer is required, also an external donor compound is added during the polymerization reaction. Both the internal and external electron donor compounds become indispensable compositions of catalyst components.

During the past 30 years, numerous supported Ziegler-Natta catalysts have been developed which afford a much higher activity in olefin polymerization reactions and much higher contents of crystalline isotactic fractions in the polymers they produce. With the development of internal and external electron donor compounds, polyolefin catalyst system is continuously renovated.

15 SUMMARY

The following presents a simplified summary in order to provide a basic understanding of some aspects of the invention. This summary is not an extensive overview of the invention. It is intended to neither identify key or critical elements of the invention nor delineate the scope of the invention. Rather, the sole purpose of this summary is to present some concepts of the invention in a simplified form.

The present disclosure provides solid catalyst components for use in olefin polymerization, olefin polymerization catalyst systems containing the solid catalyst components, methods of making the solid catalyst components and the catalyst systems, and methods of

polymerizing and copolymerizing olefins involving the use of the catalyst systems. The solid catalyst components comprise titanium, magnesium, halogen, and a combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound. The 1,8-naphthyl diester compounds include

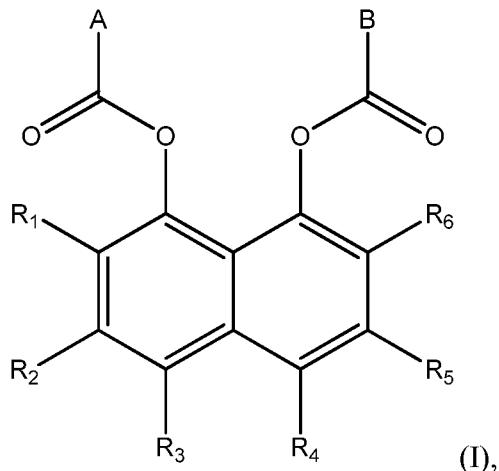
5 naphthalene-1,8-diyl dicycloalkanecarboxylate derivatives, naphthalene-1,8-diyl dicycloalkenecarboxylate derivatives, 8-(cycloalkanecarbonyloxy)naphthalene-1-yl benzoate derivatives and 8-(cycloalkenecarbonyloxy)naphthalene-1-yl benzoate derivatives. The catalyst systems can contain solid catalyst components, organoaluminum compounds, and organosilicon compounds. The solid catalyst component can be made by contacting a magnesium compound

10 and a titanium compound with a combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and/or 3,3-bis(methoxymethyl) alkane compound. The methods of polymerizing or copolymerizing olefins involve contacting olefins with catalyst systems containing a solid catalyst component, an organoaluminum compound, and an organosilicon compound.

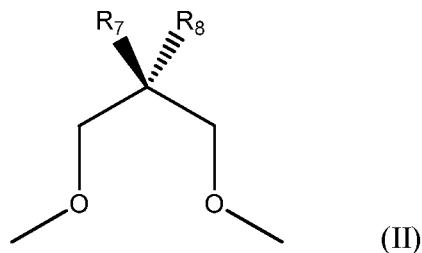
15 In an embodiment, a solid catalyst component for use in olefinic polymerization is disclosed including:

titanium,
magnesium,
halogen, and

20 a combination of internal electron donor compounds, wherein said combination of internal electron donor compounds comprises at least one 1,8-naphthyl diester compound represented by chemical formula (I):



and at least one 3,3-bis(methoxymethyl) alkane compound represented by chemical formula (II):



5

wherein

R₁-R₆ are each independently hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals;

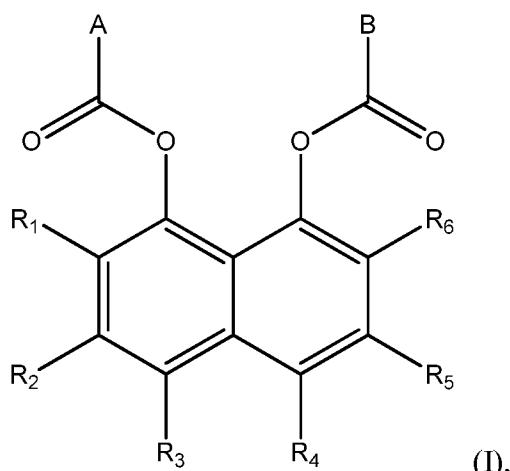
10 A and B, which are identical or different, are substituted or unsubstituted hydrocarbyl radicals having 3 to 20 carbon atoms; and

R₇ and R₈ which are identical or different, C₁-C₂₀ linear or branched alkyl, C₅-C₂₀ alkyl-cycloalkyl, or C₅-C₂₀ cycloalkyl-alkyl radicals.

In an embodiment, the solid catalyst component includes a titanium compound having at least one titanium-halogen bond and the combination of internal electron donor compounds supported on a magnesium halide crystal lattice. In an embodiment, the solid catalyst component includes a titanium compound having at least one titanium-halogen bond and the combination of 5 internal electron donor compounds supported on a magnesium dichloride crystal lattice. In an embodiment of the solid catalyst component, the titanium compound is $TiCl_4$ or $TiCl_3$.

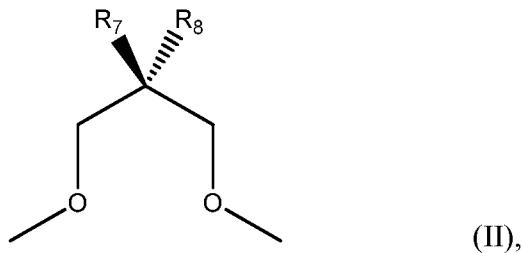
In an embodiment, a solid catalyst component for use in olefinic polymerization is disclosed, including:

10 a reaction product of a titanium compound,
a magnesium compound, and
a combination of internal electron donor compounds,
wherein said combination of internal electron donor compounds comprises at least one 15 1,8-naphthyl diester compound represented by chemical formula (I):



15 (I),

and at least one 3,3-bis(methoxymethyl) alkane compound represented by chemical formula (II):



wherein

R₁-R₆ are each independently hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals;

5

A and B, which are identical or different, are substituted or unsubstituted hydrocarbyl radicals having 3 to 20 carbon atoms; and

R₇ and R₈ which are identical or different, C₁-C₂₀ linear or branched alkyl, C₅-C₂₀ alkyl-cycloalkyl, or C₅-C₂₀ cycloalkyl-alkyl radicals. In an embodiment of the solid catalyst component, the 1,8-naphthyl diester compound of the formula (I) is selected from the group consisting of

naphthalene-8-diyl dicyclohexanecarboxylate,
 naphthalene-1,8-diyl di-2-methylcyclohexanecarboxylate,
 10 naphthalene-1,8-diyl di-3-methylcyclohexanecarboxylate,
 naphthalene-1,8-diyl di-4-methylcyclohexanecarboxylate,
 naphthalene-1,8-diyl dicyclohex-1-enecarboxylate,
 naphthalene-1,8-diyl dicyclohex-2-enecarboxylate,
 naphthalene-1,8-diyl dicyclohex-3-enecarboxylate,
 15 20 8-(cyclohexanecarbonyloxy)naphthalene-1-yl benzoate,
 8-(2-methylcyclohexanecarbonyloxy)naphthalene-1-yl benzoate,

8-(3-methylcyclohexanecarbonyloxy)naphthalene-1-yl benzoate,
8-(4-methylcyclohexanecarbonyloxy)naphthalene-1-yl benzoate,
8-(2-methylcyclohexanecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(3-methylcyclohexanecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
5 8-(4-methylcyclohexanecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(2-methylcyclohexanecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(3-methylcyclohexanecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(4-methylcyclohexanecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(2-methylcyclohexanecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
10 8-(3-methylcyclohexanecarbonyloxy)naphthalene-1-yl 4-methylbenzoate, and
8-(4-methylcyclohexanecarbonyloxy)naphthalene-1-yl 4-methylbenzoate.

In an embodiment of the solid catalyst component, the 1,8-naphthyl diester compound of the formula (I) is selected from the group consisting of

8-(cyclohex-1-enecarbonyloxy)naphthalene-1-yl benzoate,
15 8-(cyclohex-2-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(cyclohex-3-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(cyclohex-1-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(cyclohex-2-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(cyclohex-3-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
20 8-(cyclohex-1-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(cyclohex-2-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(cyclohex-3-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(cyclohex-1-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,

8-(cyclohex-2-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(cyclohex-3-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(2-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(2-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl benzoate,
5 8-(2-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(2-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(2-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(2-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(2-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
10 8-(2-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(2-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(2-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(2-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(2-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
15 8-(3-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(3-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(3-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(3-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(3-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
20 8-(3-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(3-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(3-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(3-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,

8-(3-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 4-methyl benzoate,
8-(3-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(3-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl benzoate,
5 8-(4-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(4-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(4-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(4-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 2-methyl benzoate,
10 8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(4-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 3-methyl benzoate,
8-(4-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(4-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate, and
15 8-(4-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate.

In an embodiment of the solid catalyst component, the at least one of R₇ and R₈ is C₁-C₂₀ linear or branched alkyl radicals. In an embodiment of the solid catalyst component, at least one of R₇ and R₈ is C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, or C₅-C₂₀ alkyl-cycloalkyl radicals. In an embodiment of the solid catalyst component, the at least one 3,3-20 bis(methoxymethyl) alkane compound represented by chemical formula (II) is selected from the group consisting of

1,3-dimethoxy-2,2-dimethylpropane;
1-methoxy-2-(methoxymethyl)-2-methylbutane;

1-methoxy-2-(methoxymethyl)-2-methylpentane;

1-methoxy-2-(methoxymethyl)-2-methylhexane;

1-methoxy-2-(methoxymethyl)-2-methylheptane;

1-methoxy-2-(methoxymethyl)-2-methyloctane;

5 1-methoxy-2-(methoxymethyl)-2-methylnonane;

1-methoxy-2-(methoxymethyl)-2-methyldecane;

1-methoxy-2-(methoxymethyl)-2-methylundecane;

1-methoxy-2-(methoxymethyl)-2-methyldodecane;

1-methoxy-2-(methoxymethyl)-2-methyltetradecane;

10 1-methoxy-2-(methoxymethyl)-2-methylhexadecane;

1-methoxy-2-(methoxymethyl)-2-methyloctadecane;

1-methoxy-2-(methoxymethyl)-2-methylicosane;

1-methoxy-2-(methoxymethyl)-2-methyldocosane;

1-methoxy-2-(methoxymethyl)-2,3-dimethylbutane;

15 1-methoxy-2-(methoxymethyl)-2,4-dimethylpentane;

1-methoxy-2-(methoxymethyl)-2,5-dimethylhexane;

1-methoxy-2-(methoxymethyl)-2,6-dimethylheptane;

1-methoxy-2-(methoxymethyl)-2,7-dimethyloctane;

1-methoxy-2-(methoxymethyl)-2,8-dimethylnonane;

20 1-methoxy-2-(methoxymethyl)-2,9-dimethyldecane;

1-methoxy-2-(methoxymethyl)-2,10-dimethylundecane;

1-methoxy-2-(methoxymethyl)-2,11-dimethyldodecane;

1-methoxy-2-(methoxymethyl)-2,13-dimethyltetradecane;

1-methoxy-2-(methoxymethyl)-2,15-dimethylhexadecane;

1-methoxy-2-(methoxymethyl)-2,17-dimethyloctadecane;

1-methoxy-2-(methoxymethyl)-2,19-dimethylicosane;

1-methoxy-2-(methoxymethyl)-2,21-dimethyldocosane;

5 3,3-bis(methoxymethyl)-2,4-dimethylpentane;

3,3-bis(methoxymethyl)-2,5-dimethylhexane;

3,3-bis(methoxymethyl)-2,6-dimethylheptane;

3,3-bis(methoxymethyl)-2,7-dimethyloctane;

5,5-bis(methoxymethyl)-2,9-dimethyldecane;

10 4,4-bis(methoxymethyl)-2,6-dimethylheptane;

4,4-bis(methoxymethyl)-2,7-dimethyloctane;

4,4-bis(methoxymethyl)-2,8-dimethylnonane;

5,5-bis(methoxymethyl)-2,8-dimethylnonane;

6,6-bis(methoxymethyl)-2,10-dimethylundecane;

15 3,3-bis(methoxymethyl)-2-methylpentane;

4,4-bis(methoxymethyl)-2-methylhexane;

5,5-bis(methoxymethyl)-2-methylheptane;

6,6-bis(methoxymethyl)-2-methyloctane;

6,6-bis(methoxymethyl)-2-methyldecane;

20 4,4-bis(methoxymethyl)-2-methylheptane;

5,5-bis(methoxymethyl)-2-methyloctane;

6,6-bis(methoxymethyl)-2-methylnonane;

5,5-bis(methoxymethyl)-2-methylnonane;

6,6-bis(methoxymethyl)-2-methylundecane;

3,3-bis(methoxymethyl)pentane;

3,3-bis(methoxymethyl)hexane;

3,3-bis(methoxymethyl)heptane;

5 3,3-bis(methoxymethyl)octane;

5,5-bis(methoxymethyl)decane;

4,4-bis(methoxymethyl)heptane;

4,4-bis(methoxymethyl)octane;

4,4-bis(methoxymethyl)nonane;

10 5,5-bis(methoxymethyl)nonane;

6,6-bis(methoxymethyl)undecane;

(1,3-dimethoxy-2-methylpropan-2-yl)cyclohexane;

(3-methoxy-2-(methoxymethyl)-2-methylpropyl)cyclohexane

1-(3-methoxy-2-(methoxymethyl)-2-methylpropyl)-4-methylcyclohexane;

15 1-(1,3-dimethoxy-2-methylpropan-2-yl)-4-methylcyclohexane;

(1,3-dimethoxy-2-methylpropan-2-yl)cyclopentane; and

1-(1,3-dimethoxy-2-methylpropan-2-yl)-3-methylcyclopentane.

In an embodiment, the solid catalyst component has a surface area (by B.E.T. method) between about 10 and about 1,000 m²/g.

20 In an embodiment, a catalyst system for use in olefinic polymerization is disclosed, including:

- (i) the solid catalyst component above;
- (ii) an organoaluminum compound; and

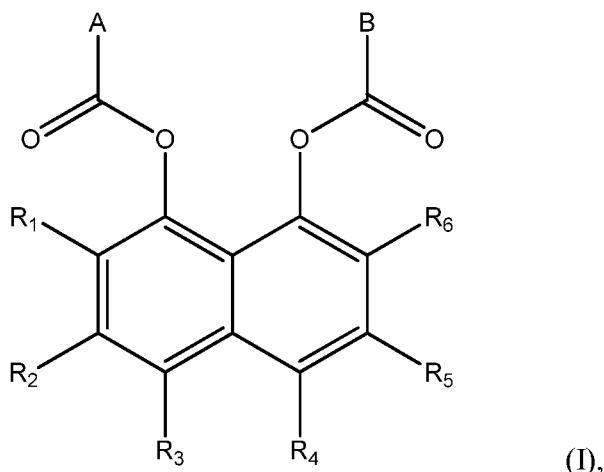
(iii) an organosilicon compound.

In an embodiment of the solid catalyst system, the organoaluminum compound is an alkyl-aluminum compound. In an embodiment of the solid catalyst system, the alkyl-aluminum compound is a trialkyl aluminum compound. In an embodiment of the solid catalyst system, 5 the trialkyl aluminum compound is selected from the group consisting of triethylaluminum, triisobutylaluminum, and tri-n-octylaluminum.

A method of making a solid catalyst component for a catalyst system is disclosed. In an embodiment, the method of making a solid catalyst component includes:

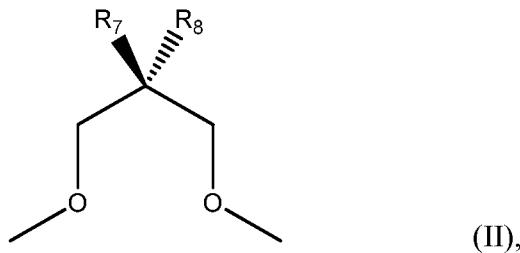
10 contacting a magnesium compound and a titanium compound with a combination of internal electron compounds,

wherein said combination of internal electron compound comprises at least one 1,8-naphthyl diester compound represented by chemical formula (I):



15

and at least one 3,3-bis(methoxymethyl) alkane compound represented by chemical formula (II):



wherein

R₁-R₆ are each independently hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀

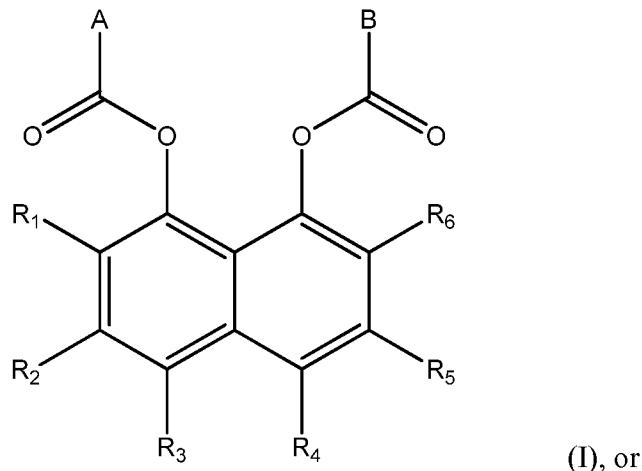
5 cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals;

A and B, which are identical or different, are substituted or unsubstituted hydrocarbyl radicals having 3 to 20 carbon atoms; and

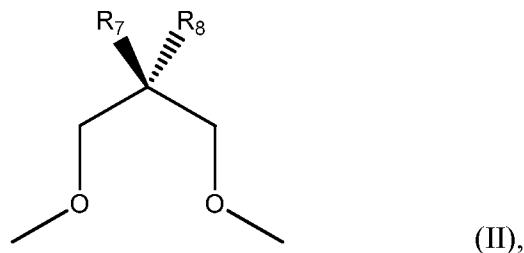
10 R₇ and R₈ which are identical or different, C₁-C₂₀ linear or branched alkyl, C₅-C₂₀ alkyl-cycloalkyl, or C₅-C₂₀ cycloalkyl-alkyl radicals.

In an embodiment of the method of making a solid catalyst component, the 1,8-naphthyl diester compound of the formula (I) is selected from the group consisting of naphthalene-1,8-diyl dicycloakanecarboxylate derivative, naphthalene-1,8-diyl dicycloalkenecarboxylate derivative, 15 8-(cycloakanecarbonyloxy)naphthalene-1-yl benzoate derivative, and 8-(cycloalkenecarbonyloxy)naphthalene-1-yl benzoate derivative.

In an embodiment, the method of making a solid catalyst component includes contacting the magnesium compound and the titanium compound with an additional internal electron donor compound, wherein said additional internal electron compound comprises at least one 1,8-20 naphthyl diester compound represented by chemical formula (I):



at least one 3,3-bis(methoxymethyl) alkane compound represented by chemical formula (II):



5

wherein

R₁-R₆ are each independently hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals;

10 A and B, which are identical or different, are substituted or unsubstituted hydrocarbyl radicals having 3 to 20 carbon atoms; and

R₇ and R₈ which are identical or different, C₁-C₂₀ linear or branched alkyl, C₅-C₂₀ alkyl-cycloalkyl, or C₅-C₂₀ cycloalkyl-alkyl radicals.

A process for polymerizing or copolymerizing an olefin monomer is disclosed. In an embodiment of the process for polymerizing or copolymerizing an olefin monomer includes the steps of:

(i) providing the catalyst system according discussed above;

5 (ii) polymerizing or copolymerizing the olefin monomer in the presence of the catalyst system to form a polymer or a copolymer; and

(iii) recovering the polymer or copolymer.

In an embodiment of the method of polymerizing or copolymerizing an olefin monomer, the olefin monomer is selected from the group consisting of ethylene, propylene, 1-butylene, 1-10 methyl-1-pentene, 1-hexene, and 1-octene.

The following description and the annexed drawings set forth in detail certain illustrative aspects and implementations of embodiments of the invention. These are indicative, however, of but a few of the various ways in which the principles of the invention may be employed. Other objects, advantages and novel features of the invention will become apparent from the following 15 detailed description of embodiments of the invention when considered in conjunction with the drawings.

BRIEF SUMMARY OF THE DRAWINGS

FIG. 1 is a high level schematic diagram of an olefin polymerization system in 20 accordance with one aspect of the present invention.

FIG. 2 is a schematic diagram of an olefin polymerization reactor in accordance with one aspect of the present invention.

FIG. 3 is a high level schematic diagram of a system for making impact copolymer in accordance with one aspect of the present invention

The drawings are exemplary only, and should not be construed as limiting the claims and embodiments provided herein.

5

DETAILED DESCRIPTION

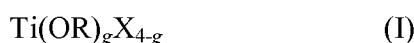
The embodiments of the present disclosure relate to solid catalyst components containing titanium, magnesium, halogen and a combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound in olefinic polymerization; olefin polymerization catalyst systems containing the solid catalyst components, organoaluminums, and organosilicons; methods of making the solid catalyst components and the catalyst systems; and methods of polymerizing and copolymerizing olefins using the catalyst systems.

An aspect includes a solid catalyst component comprising titanium, magnesium, halogen and a combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound. The 1,8-naphthyl diester compounds include naphthalene-1,8-diyl dicycloalkanecarboxylate derivatives, naphthalene-1,8-diyl dicycloalkenecarboxylate derivatives, 1,8-(cycloalkanecarbonyloxy)naphthalene-1-yl benzoate derivatives and naphthalene-1,8-diyl dicycloalkenecarboxylate derivatives. In particular, the solid catalyst component comprises a titanium compound having at least one titanium-halogen bond and a combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound supported on a magnesium halide crystal lattice.

The titanium compound is TiCl_4 or TiCl_3 . In one embodiment, the magnesium halide crystal lattice is a magnesium dichloride crystal lattice, which is widely known from the patent literature as a support for Ziegler-Natta catalysts.

Use of a combination of internal electron donor compounds containing at least one 5 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound contributes to improved performance characteristics of resultant catalysts, such as high/improved catalyst activity, high/improved hydrogen response, the ability to produce polyolefins with desired/controllable crystallinity measured by xylene soluble values and desired/controllable molecular weight measured by melt flow indexes, and the like. Combinations of mixed internal 10 donors have been disclosed in references, such as U.S. Patent No. 8,318,626. However, the present described combination of internal electron donor compounds can produce PP with very high crystallinity with and XS below 1.0. The synergetic effect between the two donor structures bonded on the catalyst surface generates active sites that favor the formation of a highly isotactic polypropylene chain.

15 The solid catalyst component of an embodiment of the present disclosure is a highly active catalyst component comprising a reaction product of a titanium compound, a magnesium compound, and a combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound. The titanium compounds used in the preparation of the solid catalyst component include, for 20 example, a tetravalent titanium compound represented by chemical formula (I):



wherein R represents a hydrocarbon group, preferably an alkyl group having 1 to about 20 carbon atoms, X represents a halogen atom, and $0 \leq g \leq 4$. Specific examples of the titanium

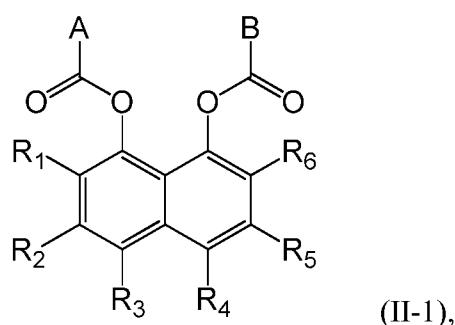
compound include, but are not limited to titanium tetrahalides such as $TiCl_4$, $TiBr_4$ and TiI_4 ; alkoxytitanium trihalides such as $Ti(OCH_3)Cl_3$, $Ti(OC_2H_5)Cl_3$, $Ti(O-n-C_4H_9)Cl_3$, $Ti(OC_2H_5)Br_3$ and $Ti(O-i-C_4H_9)Br_3$; dialkoxytitanium dihalides such as $Ti(OCH_3)_2Cl_2$, $Ti(OC_2H_5)_2Cl_2$, $Ti(O-n-C_4H_9)_2Cl_2$ and $Ti(OC_2H_5)_2Br_2$; trialkoxytitanium monohalides such as $Ti(OCH_3)_3Cl$, $Ti(OC_2H_5)_3Cl$, $Ti(O-n-C_4H_9)_3Cl$ and $Ti(OC_2H_5)_3Br$; and tetraalkoxytitaniums such as $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$ and $Ti(O-n-C_4H_9)_4$. Among these, the halogen containing titanium compounds, especially titanium tetrahalides, are preferred in some instances. These titanium compounds may be used individually or in solutions of hydrocarbon compounds or halogenated hydrocarbons.

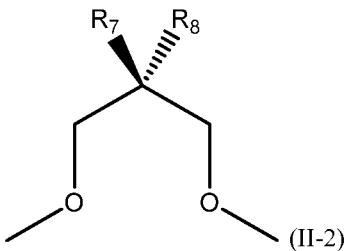
The magnesium compounds used in the preparation of the solid catalyst component include, for example, a magnesium compound having no reducibility. In one embodiment, the magnesium compound having no reducibility is a halogen containing magnesium compound. Specific examples of the magnesium compound having no reducibility include, but are not limited to magnesium halides, such as magnesium chloride, magnesium bromide, magnesium iodide and magnesium fluoride; alkoxy magnesium halides, such as methoxy magnesium chloride, ethoxy magnesium chloride, isopropoxy magnesium chloride, butoxy magnesium chloride and octoxy magnesium chloride; aryloxy magnesium halides, such as phenoxy magnesium chloride and methylphenoxy magnesium chloride; alkoxy magnesiums, such as ethoxy magnesium, isopropoxy magnesium, butoxy magnesium, n-octoxy magnesium and 2-ethylhexoxy magnesium; aryloxy magnesiums, such as phenoxy magnesium and dimethylphenoxy magnesium; and carboxylic acid salts of magnesium, such as magnesium laurate and magnesium stearate. These magnesium compounds may be in the liquid or solid state.

In one aspect, halogen containing magnesium compounds, such as magnesium chloride, alkoxy magnesium chlorides and aryloxy magnesium chlorides, are employed.

When preparing the solid catalyst component, a combination of internal electron donors can be used/added. The solid titanium catalyst component can be made by contacting a 5 magnesium compound and a titanium compound with a combination of internal electron donor compounds. In one embodiment, the solid titanium catalyst component is made by contacting a magnesium compound and a titanium compound in the presence of a combination of internal electron donor compounds. In another embodiment, the solid titanium catalyst component is made by forming a magnesium based catalyst support optionally with the titanium compound 10 and optionally with the combination of internal electron donor compounds, and contacting the magnesium based catalyst support with the titanium compound and the combination of internal electron donor compounds. It is understood that at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound can be added in either order, or simultaneously.

15 The combination of internal electron donor compounds comprises at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound. The general structure of the combination of internal electron donor compounds is represented by the following chemical formulas (II-1) and (II-2):





wherein,

R₁-R₆ are each independently hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals;

5

A and B, which are identical or different, are substituted or unsubstituted hydrocarbyl radicals having 3 to 20 carbon atoms; and

10 R₇ and R₈ which are identical or different, are C₁-C₂₀ linear or branched alkyl, C₅-C₂₀ alkyl-cycloalkyl, or C₅-C₂₀ cycloalkyl-alkyl radicals.

In some embodiments, R₁ is hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals.

In some embodiments, R₁ is hydrogen, or C₁-C₂₀ linear or branched alkyl radicals.

15 In some embodiments, R₁ is hydrogen, or C₁-C₁₀ linear or branched alkyl radicals.

In some embodiments, R₂ is hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals.

In some embodiments, R₂ is hydrogen, or C₁-C₂₀ linear or branched alkyl radicals.

In some embodiments, R₂ is hydrogen, or C₁-C₁₀ linear or branched alkyl radicals.

20 In some embodiments, R₃ is hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals.

In some embodiments, R₃ is hydrogen, or C₁-C₂₀ linear or branched alkyl radicals.

In some embodiments, R₃ is hydrogen, or C₁-C₁₀ linear or branched alkyl radicals.

In some embodiments, R₄ is hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals.

5 In some embodiments, R₄ is hydrogen, or C₁-C₂₀ linear or branched alkyl radicals.

In some embodiments, R₄ is hydrogen, or C₁-C₁₀ linear or branched alkyl radicals.

In some embodiments, R₅ is hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals.

In some embodiments, R₅ is hydrogen, or C₁-C₂₀ linear or branched alkyl radicals.

10 In some embodiments, R₅ is hydrogen, or C₁-C₁₀ linear or branched alkyl radicals.

In some embodiments, R₆ is hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals.

In some embodiments, R₆ is hydrogen, or C₁-C₂₀ linear or branched alkyl radicals.

In some embodiments, R₆ is hydrogen, or C₁-C₁₀ linear or branched alkyl radicals.

15 In some embodiments, “A” are substituted or unsubstituted hydrocarbyl-radicals having 3 to 20 carbon atoms.

In some embodiments, “A” is C₃-C₂₀ linear or branched alkyl, C₅-C₂₀ cycloalkyl, C₅-C₂₀ cycloalkenyl, C₅-C₂₀ cyclodialkenyl, phenyl, C₇-C₁₈ alkylaryl, or C₇-C₁₈ arylalkyl radicals.

20 In some embodiments, “A” is C₃-C₂₀ linear or branched alkyl, C₅-C₂₀ cycloalkyl, or C₅-C₂₀ cycloalkenyl.

In some embodiments, “B” are substituted or unsubstituted hydrocarbyl radicals having 3 to 20 carbon atoms.

In some embodiments, “B” is C₃-C₂₀ linear or branched alkyl, C₅-C₂₀ cycloalkyl, C₅-C₂₀ cycloalkenyl, C₅-C₂₀ cyclodialkenyl, phenyl, C₇-C₁₈ alkylaryl, or C₇-C₁₈ arylalkyl radicals.

In some embodiments, “B” is C₃-C₂₀ linear or branched alkyl, C₅-C₂₀ cycloalkyl, or C₅-C₂₀ cycloalkenyl radicals.

5 In some embodiments, R₇ is C₁-C₂₀ linear or branched alkyl, C₅-C₂₀ alkyl-cycloalkyl, or C₅-C₂₀ cycloalkyl-alkyl radicals.

In some embodiments, R₇ is C₁-C₂₀ linear or branched alkyl, or C₅-C₂₀ cycloalkyl-alkyl radicals.

10 In some embodiments, R₇ is C₁-C₂₀ linear or branched alkyl, or C₅-C₂₀ alkyl-cycloalkyl radicals.

In some embodiments, R₇ is C₁-C₂₀ linear or branched alkyl radicals.

In some embodiments, R₇ is C₁-C₂₀ branched alkyl radicals having 1, 2, or 3 branches.

In some embodiments, R₇ is C₁-C₁₀ linear or branched alkyl radicals.

In some embodiments, R₇ is C₁-C₁₀ branched alkyl radicals having 1, 2, or 3 branches.

15 In some embodiments, R₈ is C₁-C₂₀ linear or branched alkyl, C₅-C₂₀ alkyl-cycloalkyl, or C₅-C₂₀ cycloalkyl-alkyl radicals.

In some embodiments, R₈ is C₁-C₂₀ linear or branched alkyl, or C₅-C₂₀ cycloalkyl-alkyl radicals.

20 In some embodiments, R₈ is C₁-C₂₀ linear or branched alkyl, or C₅-C₂₀ alkyl-cycloalkyl radicals.

In some embodiments, R₈ is C₁-C₂₀ linear or branched alkyl radicals.

In some embodiments, R₈ is C₁-C₂₀ branched alkyl radicals having 1, 2, or 3 branches.

In some embodiments, R₈ is C₁-C₁₀ linear or branched alkyl radicals.

In some embodiments, R₈ is C₁-C₁₀ branched alkyl radicals having 1, 2, or 3 branches.

The term “hydrocarbyl” refers to any moiety comprising only hydrogen and carbon atoms, unless otherwise explicitly stated. A hydrocarbyl can also form a non-aromatic, such as cyclohexane, or an aromatic ring, such as a substituted or unsubstituted (C₆-C₁₀)aryl group.

5 Preferred hydrocarbyl groups are (C₃-C₂₀)hydrocarbyl, more preferred are (C₃-C₁₀)hydrocarbyl, and most preferred are benzyl and cyclohexyl.

The term “radicals” as used herein refers to a substituent. For example, the phrase alkyl radical indicates that an alkyl is substituted into a given formula as a substituent.

10 The 1,8-naphthyl diester compound comprises naphthalene-1,8-diyl dicycloalkanecarboxylate derivatives, naphthalene-1,8-diyl dicycloalkenecarboxylate derivatives, 8-(cycloalkanecarbonyloxy)naphthalene-1-yl benzoate derivatives and 8-(cycloalkenecarbonyloxy)naphthalene-1-yl benzoate derivatives.

15 Specific examples of naphthalene-8-diyl dicycloalkanecarboxylate derivatives include, but are not limited to naphthalene-8-diyl dicyclohexanecarboxylate, naphthalene-1,8-diyl di-2-methylcyclohexanecarboxylate, naphthalene-1,8-diyl di-3-methylcyclohexanecarboxylate, and naphthalene-1,8-diyl di-4-methylcyclohexanecarboxylate.

Specific examples of naphthalene-1,8-diyl dicycloalkenecarboxylate derivatives include, but are not limited to naphthalene-1,8-diyl dicyclohex-1-enecarboxylate, naphthalene-1,8-diyl dicyclohex-2-enecarboxylate, and naphthalene-1,8-diyl dicyclohex-3-enecarboxylate.

20 Specific examples of 8-(cycloalkanecarbonyloxy)naphthalene-1-yl benzoate derivatives include, but are not limited to 8-(cyclohexanecarbonyloxy)naphthalene-1-yl benzoate, 8-(2-methylcyclohexanecarbonyloxy)naphthalene-1-yl benzoate, 8-(3-methylcyclohexanecarbonyloxy) naphthalene-1-yl benzoate,

8-(4-methylcyclohexanecarbonyloxy)naphthalene-1-yl benzoate,
8-(2-methylcyclohexanecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(3-methylcyclohexanecarbonyloxy) naphthalene-1-yl 2-methylbenzoate,
8-(4-methylcyclohexanecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
5 8-(2-methylcyclohexanecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(3-methylcyclohexanecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(2-methylcyclohexanecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(3-methylcyclohexanecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
10 and 8-(4-methylcyclohexanecarbonyloxy)naphthalene-1-yl 4-methylbenzoate.

Specific examples of 8-(cycloalkenecarbonyloxy)naphthalene-1-yl benzoate derivatives include, but are not limited to 8-(cyclohex-1-enecarbonyloxy)naphthalene-1-yl benzoate, 8-(cyclohex-2-enecarbonyloxy)naphthalene-1-yl benzoate, 8-(cyclohex-3-enecarbonyloxy)naphthalene-1-yl benzoate, 15 8-(cyclohex-1-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate, 8-(cyclohex-2-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate, 8-(cyclohex-3-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate, 8-(cyclohex-1-enecarbonyloxy)naphthalene-1-yl 3 methylbenzoate, 8-(cyclohex-2-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate, 20 8-(cyclohex-3-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate, 8-(cyclohex-1-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate, 8-(cyclohex-2-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate, 8-(cyclohex-3-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,

8-(2-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(2-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(2-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(2-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
5 8-(2-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(2-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(2-methylcyclohex-1-enecarbonyloxy) naphthalene-1-yl 3-methylbenzoate,
8-(2-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(2-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
10 8-(2-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(2-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(2-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(3-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(3-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl benzoate,
15 8-(3-methylcyclohex 3-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(3-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(3-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(3-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(3-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
20 8-(3-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(3-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(3-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(3-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,

8-(3-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,

8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl benzoate,

8-(4-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl benzoate,

8-(4-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl benzoate,

5 8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,

8-(4-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,

8-(4-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,

8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,

8-(4-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,

10 8-(4-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,

8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,

8-(4-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,

and 8-(4-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate.

Examples of 3,3-bis(methoxymethyl) alkane compound include, but are not limited to

15 1,3-dimethoxy-2,2-dimethylpropane;

1-methoxy-2-(methoxymethyl)-2-methylbutane;

1-methoxy-2-(methoxymethyl)-2-methylpentane;

1-methoxy-2-(methoxymethyl)-2-methylhexane;

1-methoxy-2-(methoxymethyl)-2-methylheptane;

20 1-methoxy-2-(methoxymethyl)-2-methyloctane;

1-methoxy-2-(methoxymethyl)-2-methylnonane;

1-methoxy-2-(methoxymethyl)-2-methyldecane;

1-methoxy-2-(methoxymethyl)-2-methylundecane;

1-methoxy-2-(methoxymethyl)-2-methyldodecane;

1-methoxy-2-(methoxymethyl)-2-methyltetradecane;

1-methoxy-2-(methoxymethyl)-2-methylhexadecane;

5 1-methoxy-2-(methoxymethyl)-2-methyloctadecane;

1-methoxy-2-(methoxymethyl)-2-methylicosane;

1-methoxy-2-(methoxymethyl)-2-methyldocosane;

1-methoxy-2-(methoxymethyl)-2,3-dimethylbutane;

1-methoxy-2-(methoxymethyl)-2,4-dimethylpentane;

10 1-methoxy-2-(methoxymethyl)-2,5-dimethylhexane;

1-methoxy-2-(methoxymethyl)-2,6-dimethylheptane;

1-methoxy-2-(methoxymethyl)-2,7-dimethyloctane;

1-methoxy-2-(methoxymethyl)-2,8-dimethylnonane;

1-methoxy-2-(methoxymethyl)-2,9-dimethyldecane;

15 1-methoxy-2-(methoxymethyl)-2,10-dimethylundecane;

1-methoxy-2-(methoxymethyl)-2,11-dimethyldodecane;

1-methoxy-2-(methoxymethyl)-2,13-dimethyltetradecane;

1-methoxy-2-(methoxymethyl)-2,15-dimethylhexadecane;

1-methoxy-2-(methoxymethyl)-2,17-dimethyloctadecane;

1-methoxy-2-(methoxymethyl)-2,19-dimethylicosane;

1-methoxy-2-(methoxymethyl)-2,21-dimethyldocosane;

5 3,3-bis(methoxymethyl)-2,4-dimethylpentane;

3,3-bis(methoxymethyl)-2,5-dimethylhexane;

3,3-bis(methoxymethyl)-2,6-dimethylheptane;

3,3-bis(methoxymethyl)-2,7-dimethyloctane;

5,5-bis(methoxymethyl)-2,9-dimethyldecane;

10 4,4-bis(methoxymethyl)-2,6-dimethylheptane;

4,4-bis(methoxymethyl)-2,7-dimethyloctane;

4,4-bis(methoxymethyl)-2,8-dimethylnonane;

5,5-bis(methoxymethyl)-2,8-dimethylnonane;

6,6-bis(methoxymethyl)-2,10-dimethylundecane;

15 3,3-bis(methoxymethyl)-2-methylpentane;

4,4-bis(methoxymethyl)-2-methylhexane;

5,5-bis(methoxymethyl)-2-methylheptane;

6,6-bis(methoxymethyl)-2-methyloctane;

6,6-bis(methoxymethyl)-2-methyldecane;

4,4-bis(methoxymethyl)-2-methylheptane;

5,5-bis(methoxymethyl)-2-methyloctane;

5 6,6-bis(methoxymethyl)-2-methylnonane;

5,5-bis(methoxymethyl)-2-methylnonane;

6,6-bis(methoxymethyl)-2-methylundecane;

3,3-bis(methoxymethyl)pentane;

3,3-bis(methoxymethyl)hexane;

10 3,3-bis(methoxymethyl)heptane;

3,3-bis(methoxymethyl)octane;

5,5-bis(methoxymethyl)decane;

4,4-bis(methoxymethyl)heptane;

4,4-bis(methoxymethyl)octane;

15 4,4-bis(methoxymethyl)nonane;

5,5-bis(methoxymethyl)nonane;

6,6-bis(methoxymethyl)undecane;

(1,3-dimethoxy-2-methylpropan-2-yl)cyclohexane;

(3-methoxy-2-(methoxymethyl)-2-methylpropyl)cyclohexane

1-(3-methoxy-2-(methoxymethyl)-2-methylpropyl)-4-methylcyclohexane;

1-(1,3-dimethoxy-2-methylpropan-2-yl)-4-methylcyclohexane;

5 (1,3-dimethoxy-2-methylpropan-2-yl)cyclopentane; and

1-(1,3-dimethoxy-2-methylpropan-2-yl)-3-methylcyclopentane.

In one embodiment, the solid catalyst component comprises the combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound, but does not include other internal electron 10 donors. In another embodiment, the solid catalyst component includes other internal electron donors in addition to the combination of internal electron donor containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound. For example, when preparing the solid catalyst component, other internal electron donors can be used/added in addition to the combination of internal electron donors containing at least one 15 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound.

Examples of other internal electron donors include oxygen-containing electron donors such as organic acid esters. Specific examples include, but are not limited to diethyl ethylmalonate, diethyl propylmalonate, diethyl isopropylmalonate, diethyl butylmalonate, diethyl 1,2-cyclohexanedicarboxylate, di-2-ethylhexyl-1,2-cyclohexanedicarboxylate, di-2-isononyl 20 1,2-cyclohexanedicarboxylate, methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, octyl benzoate, cyclohexyl benzoate, phenyl benzoate, benzyl benzoate, methyl toluate, ethyl

toluate, amyl toluate, ethyl ethylbenzoate, methyl anisate, ethyl anisate, ethyl ethoxybenzoate, diisononyl phthalate, di-2-ethylhexyl phthalate, diethyl succinate, dipropyl succinate, diisopropyl succinate, dibutyl succinate, diisobutyl succinate, dioctyl succinate, diisononyl succinate, and diether compounds such as 9,9-bis (methoxymethyl)fluorine, 2-isopropyl-2-isopentyl-1, 5 3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-diisopentyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane.

The combination of internal electron donor compounds may be used individually or in combination. In employing the internal electron donor compounds, they do not have to be used directly as starting materials, but compounds convertible to the electron donors in the course of 10 preparing the solid catalyst components may also be used as the starting materials.

The solid catalyst component can be made by contacting a magnesium compound and a titanium compound with a combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane.

In one embodiment, the solid catalyst component is made by contacting a magnesium 15 compound and a titanium compound in the presence of a combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane. In another embodiment, the solid catalyst component is made by forming a magnesium based catalyst support/catalyst crystal lattice optionally with a titanium compound and optionally with a combination of internal electron donor compounds containing at 20 least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane, and contacting the magnesium based catalyst support/catalyst crystal lattice with the titanium compound and the combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane. In yet another

embodiment, the solid catalyst component is made by contacting a magnesium based catalyst support/catalyst crystal lattice with a titanium compound to form a mixture, then contacting the mixture with a combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane. In still yet 5 another embodiment, the solid catalyst component is made by contacting a magnesium based catalyst support/catalyst crystal lattice with a titanium compound to form a mixture, then contacting the mixture with a combination of internal electron compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane, then contacting the mixture again with the combination of internal electron donor compounds containing at least 10 one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane. Such repeated contact with the combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane can occur once, twice, three times, four times or more, successively or with other acts performed between contacts with additional doses of the internal electron donor compounds containing at least one 15 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane. It is understood that the at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane discussed in the procedures above can be added in any order or simultaneously. Further, where one of the at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane is described above as added during a step, then the other can be 20 added during later step, so long as both function as both are added to produce a functioning catalyst.

Generally speaking, the magnesium based catalyst support/catalyst crystal lattice is made by dissolving a magnesium compound in a solvent mixture comprising an organic epoxy

compound, an organic phosphorus compound and an optional inert diluent to form a homogenous solution.

The organic epoxy compounds used in the embodiments of present invention include compounds having at least one epoxy group in the forms of monomers, dimmers, oligomers and 5 polymers. Examples of epoxy compounds include, but are not limited to aliphatic epoxy compounds, alicyclic epoxy compounds, aromatic epoxy compounds, or the like. Examples of aliphatic epoxy compounds include, but are not limited to halogenated aliphatic epoxy compounds, aliphatic epoxy compounds having a keto group, aliphatic epoxy compounds having an ether bond, aliphatic epoxy compounds having an ester bond, aliphatic epoxy compounds 10 having a tertiary amino group, aliphatic epoxy compounds having a cyano group, or the like. Examples of alicyclic epoxy compounds include, but are not limited to halogenated alicyclic epoxy compounds, alicyclic epoxy compounds having a keto group, alicyclic epoxy compounds having an ether bond, alicyclic epoxy compounds having an ester bond, alicyclic epoxy compounds having a tertiary amino group, alicyclic epoxy compounds having a cyano group, or 15 the like. Examples of aromatic epoxy compounds include, but are not limited to halogenated aromatic epoxy compounds, aromatic epoxy compounds having a keto group, aromatic epoxy compounds having an ether bond, aromatic epoxy compounds having an ester bond, aromatic epoxy compounds having a tertiary amino group, aromatic epoxy compounds having a cyano group, or the like.

20 Specific examples of epoxy compounds include, but are not limited to epifluorohydrin, epichlorohydrin, epibromohydrin, hexafluoropropylene oxide, 1,2-epoxy-4-fluorobutane, 1-(2,3-epoxypropyl)-4-fluorobenzene, 1-(3,4-epoxybutyl)-2-fluorobenzene, (epoxypropyl)-4-chlorobenzene, 1-(3,4-epoxybutyl)-3-chlorobenzene, or the like. Specific

examples of halogenated alicyclic epoxy compounds include 4-fluoro-1,2-cyclohexene oxide, 6-chloro-2,3 epoxybicyclo [2,2,1]heptane, or the like. Specific examples of halogenated aromatic epoxy compounds include 4-fluorostyrene oxide, 1-(1,2-epoxypropyl)-3-trifluorobenzene, or the like.

5 The organic phosphorus compounds used in embodiments of the present invention include, but are not limited to hydrocarbyl esters and halohydrocarbyl esters of ortho-phosphoric acid and phosphorous acid. Specific examples include, but are not limited to trimethyl phosphate, triethyl phosphate, tributyl phosphate, triphenyl phosphate, trimethyl phosphite, triethyl phosphite, tributyl phosphite and triphenyl phosphite.

10 For more sufficiently dissolving a magnesium compound, an inert diluent is optionally added in the solvent mixture. The inert diluent can typically be aromatic hydrocarbons or alkanes, as long as it can facilitate the dissolution of the magnesium compound. Examples of aromatic hydrocarbons include, but are not limited to benzene, toluene, xylene, chlorobenzene, dichlorobenzene, trichlorobenzene, chlorotoluene, and derivatives thereof. Examples of alkanes 15 include linear, branched, or cyclic alkanes having about 3 to about 30 carbons, such as butane, pentane, hexane, cyclohexane, heptanes, and the like. These inert diluents may be used alone or in combination.

20 In embodiments of making the solid catalyst component according to the Examples, the magnesium based catalyst support/catalyst crystal lattice is mixed with a titanium compound such as liquid titanium tetrahalide to form a solid precipitate in the optional presence of an auxiliary precipitant. The auxiliary precipitant may be added before, during or after the precipitation of the solids and loaded on the solids.

The auxiliary precipitants used in embodiments of the present invention include carboxylic acids, carboxylic acid anhydrides, ethers, ketones, or mixture thereof. Specific examples include, but are not limited to acetic anhydride, phthalic anhydride, succinic anhydride, maleic anhydride, 1,2,4,5-benzene tetracarboxylic dianhydride, acetic acid, propionic acid, 5 butyric acid, acrylic acid, methacrylic acid, acetone, methyl ethyl ketone, benzophenone, dimethyl ether, diethyl ether, dipropyl ether, dibutyl ether, and dipentyl ether.

The process of solids precipitation can be carried out by at least one of three methods. One method involves mixing a titanium compound such as liquid titanium tetrahalide with a magnesium based catalyst support/catalyst crystal lattice at a temperature in the range of about 10 -40 degrees Celsius to about 0 degrees Celsius, and precipitating the solids while the temperature is raised slowly to a range from about 30 degrees Celsius to about 120 degrees Celsius, such as from about 60 degrees Celsius to about 100 degrees Celsius. The second method involves adding a titanium compound dropwise into a magnesium based catalyst support/catalyst crystal lattice at low or room temperature to precipitate out solids immediately. The third method 15 involves adding a first titanium compound dropwise into a magnesium based catalyst support/catalyst crystal lattice and mixing a second titanium compound with the magnesium catalyst support/catalyst crystal lattice. In these methods, a combination of an internal electron donor compounds can be desirably present in the reaction system. The combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least 20 one 3,3-bis(methoxymethyl) alkane can be added, either after the magnesium based catalyst support/catalyst crystal lattice is obtained or after the solid precipitate is formed. Further, it is understood that the at least one 1,8-naphthyl diester compound and at least one 3,3-

bis(methoxymethyl) alkane discussed in the procedures above can be added in any order or simultaneously.

In one embodiment, when the solid catalyst component is formed, a surfactant can be used. The surfactant can contribute to many of the beneficial properties of the solid catalyst component and catalyst system. General examples of surfactants include polymer surfactants, such as polyacrylates, polymethacrylates, polyalkyl methacrylates, and the like. A polyalkyl methacrylate is a polymer that may contain one or more methacrylate monomers, such as at least two different methacrylate monomers, at least three different methacrylate monomers, etc. Moreover, the acrylate and methacrylate polymers may contain monomers other than acrylate and methacrylate monomers, so long as the polymer surfactant contains at least about 40% by weight acrylate and methacrylate monomers.

In one embodiment, non-ionic surfactants and/or anionic surfactants can be used. Examples of non-ionic surfactants and/or anionic surfactants include, but are not limited to phosphate esters, alkyl sulfonates, aryl sulfonates, alkylaryl sulfonates, linear alkyl benzene sulfonates, alkylphenols, ethoxylated alcohols, carboxylic esters, fatty alcohols, fatty esters, fatty aldehydes, fatty ketones, fatty acid nitrites, benzene, naphthalene, anthracene, succinic anhydride, phthalic anhydrides, rosin, terpene, phenol, or the like. In fact, a number of anhydride surfactants are effective. In some instances, the absence of an anhydride surfactant causes the formation of very small catalyst support particles while the over-use creates straw shaped material sometimes referred to as needles.

The solid catalyst precursor can be formed in the following way. In a solvent such as toluene, a magnesium and titanium containing solution is seen following the addition of a halogenating agent such as $TiCl_4$ into a magnesium based solution at relatively cooler

temperatures, such as -25 degrees Celsius until about 0 degrees Celsius. An oil phase is then formed, which can be dispersed into the hydrocarbon phase that is stable until about 40 degrees Celsius. The resultant magnesium material becomes a semi-solid at this point and the particle morphology is now determined. The semisolid converts to a solid between about 40 degrees

5 Celsius and about 80 degrees Celsius.

To facilitate obtaining uniform solid particles, the process of precipitation can be carried out slowly. When the second method of adding titanium halide dropwise at low or room temperature is applied, the process may take place over a period from about 1 hour to about 6 hours. When the first method of raising the temperature in a slow manner is applied, the rate of

10 temperature increase can range from about 4 degrees Celsius to about 125 degrees Celsius per hour.

The solid precipitate is first separated from the mixture. In the solid precipitate thus obtained may be entrained a variety of complexes and byproducts, so that further treatment may in some instances be necessary. In one embodiment, the solid precipitate is treated with a

15 titanium compound to substantially remove the byproducts from the solid precipitate.

The solid precipitate can be washed with an inert diluent and then treated with a titanium compound or a combination of a titanium compound and an inert diluent. The titanium compound used in this treatment can be identical to or different with the titanium compound used for forming the solid precipitate. The amount of titanium compound used is from about 1 to

20 about 20 moles, such as from about 2 to about 15 moles, per mole of magnesium compound in the support. The treatment temperature ranges from about 50 degrees Celsius to about 150 degrees Celsius, such as from about 60 degrees Celsius to about 100 degrees Celsius. If a combination of titanium tetrahalide and an inert diluent is used to treat the solid precipitate, the

volume % of titanium tetrahalide in the treating solution is from about 10% to about 100%, the rest being the inert diluent.

The treated solids can be further washed with an inert diluent to remove ineffective titanium compounds and other byproducts. The inert diluent herein used can be hexane, 5 heptanes, octane, 1,2-dichloroethane, benzene, toluene, ethylbenzene, xylene, and other hydrocarbons.

By treating the solid precipitate with the titanium compound and optionally an inert diluent, the byproducts in the solid precipitate can be removed from the solid precipitate. In one embodiment, the solid precipitate is treated with the titanium compound and optionally an inert 10 diluent about two times or more and five times or less.

By treating the solid precipitate with an inert diluent, a free titanium compound in the solid precipitate can be removed from the solid precipitate. As a result, the resultant solid precipitate does not substantially contain a free titanium compound. In one embodiment, the solid precipitate is treated repeatedly with an inert diluent until the filtrate contains about 100 15 ppm or less of titanium. In another embodiment, the solid precipitate is treated repeatedly with an inert diluent until the filtrate contains about 50 ppm or less of titanium. In yet another embodiment, the solid precipitate is treated with an inert diluent until the filtrate contains about 10 ppm or less of titanium. In one embodiment, the solid precipitate is treated with an inert diluent about three times or more and seven times or less.

20 In one embodiment, the solid catalyst component contains from about 0.5 to about 6.0 wt % titanium; from about 10 to about 25 wt % magnesium; from about 40 to about 70 wt % halogen; from about 1 to about 50 wt % the combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl)

alkane; and optionally inert diluent from about 0 to about 15 wt %. In another embodiment, the solid catalyst component contains from about 2 to about 25 wt % of one or more of the combination of internal electron donors containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane. In yet another embodiment, the solid catalyst 5 component contains from about 5 to about 20 wt % of one or more of the combination of internal electron donors containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane at least one 3,3-bis(methoxymethyl) alkane compound.

The amounts of the ingredients used in preparing the solid catalyst component may vary depending upon the method of preparation. In one embodiment, from about 0.01 to about 10 10 moles of the internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane, and from about 0.01 to about 500 moles of the titanium compounds are used per mole of the magnesium compound used to make the solid catalyst component. In an embodiment, the amount of at least one 1,8-naphthyl diester compound can be from about 0.01 to about 7 moles, including 0.5-5 moles. In an embodiment, 15 the amount of at least one 3,3-bis(methoxymethyl) alkane can be from about 0.01 to about 7 moles, including 0.5-5 moles. In another embodiment, from about 0.05 to about 2 moles of the combination of internal electron donor compounds containing at least one 1,8-naphthyl diester compound and at least one 3,3-bis(methoxymethyl) alkane compound, and from about 0.05 to about 300 moles of the titanium compounds are used per mole of the magnesium compound used 20 to make the solid catalyst component.

In one embodiment, in the solid catalyst component, the atomic ratio of halogen/titanium is from about 4 to about 200; the combination of internal electron donor/titanium mole ratio is from about 0.01 to about 10; and the magnesium/titanium atomic ratio is from about 1 to about

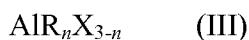
100. In another embodiment, in the solid catalyst component, the atomic ratio of halogen/titanium is from about 5 to about 100; the combination of internal electron donor/titanium mole ratio is from about 0.2 to about 6; and the magnesium/titanium atomic ratio is from about 2 to about 50.

5 The resulting solid catalyst component generally contains a magnesium halide of a smaller crystal size than commercial magnesium halides and usually has a specific surface area of at least about 5 m²/g, such as from about 10 to about 1,000 m²/g, or from about 100 to about 800 m²/g. Since the above ingredients are unified to form an integral structure of the solid catalyst component, the composition of the solid catalyst component does not substantially 10 change by washing with, for example, hexane.

The solid catalyst component may be used after being diluted with an inorganic or organic compound such as a silicon compound, an aluminum compound, or the like.

Methods of preparing solid catalyst components, which can be used in the embodiments of present invention, are described in U.S. Pat. Nos. 4,771,023; 4,784,983; 4,829,038; 4,861,847; 15 4,990,479; 5,177,043; 5,194,531; 5,244,989; 5,438,110; 5,489,634; 5,576,259; 5,767,215; 5,773,537; 5,905,050; 6,323,152; 6,437,061; 6,469,112; 6,962,889; 7,135,531; 7,153,803; 7,271,119; U.S. Patent Publication Nos: 2004242406; 20040242407; and 20070021573 which are hereby incorporated by reference in this regard.

20 The catalyst system may contain at least one organoaluminum compound in addition to the solid catalyst component. Compounds having at least one aluminum-carbon bond in the molecule can be used as the organoaluminum compound. Examples of organoaluminum compounds include compounds of the following chemical formula (III):



In formula (III), R independently represents a hydrocarbon group usually having 1 to about 20 carbon atoms, X represents a halogen atom, and $0 < n \leq 3$.

Specific examples of the organoaluminum compounds represented by formula (III) include, but are not limited to trialkyl aluminums, such as triethyl aluminum, tributyl aluminum and trihexyl aluminum; trialkenyl aluminums, such as triisoprenyl aluminum; dialkyl aluminum halides, such as diethyl aluminum chloride, dibutyl aluminum chloride and diethyl aluminum bromide; alkyl aluminum sesquihalides, such as ethyl aluminum sesquichloride, butyl aluminum sesquichloride and ethyl aluminum sesquibromide; alkyl aluminum dihalides, such as ethyl aluminum dichloride, propyl aluminum dichloride and butyl aluminum dibromide; dialkyl aluminum hydrides, such as diethyl aluminum hydride and dibutyl aluminum hydride; and other partially hydrogenated alkyl aluminum, such as ethyl aluminum dihydride and propyl aluminum dihydride.

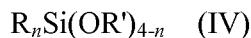
The organoaluminum compound is used in the catalyst system of embodiments of the present invention in an amount that the mole ratio of aluminum to titanium (from the solid catalyst component) is from about 5 to about 1,000. In another embodiment, the mole ratio of aluminum to titanium in the catalyst system is from about 10 to about 700. In yet another embodiment, the mole ratio of aluminum to titanium in the catalyst system is from about 25 to about 400.

The catalyst system may contain at least one organosilicon compound in addition to the solid catalyst component. This organosilicon compound is sometimes termed as an external electron donor. The organosilicon compound contains silicon having at least one hydrogen ligand (hydrocarbon group). General examples of hydrocarbon groups include alkyl groups, cycloalkyl groups, (cycloalkyl) methylene groups, alkene groups, aromatic groups, and the like.

The organosilicon compound, when used as an external electron donor serving as one component of a Ziegler-Natta catalyst system for olefin polymerization, contributes to the ability to obtain a polymer (at least a portion of which is polyolefin) having a controllable molecular weight distribution and controllable crystallinity while retaining high performance with respect to catalytic activity.

The organosilicon compound is used in the catalyst system in an amount that the mole ratio of the organoaluminum compound to the organosilicon compound is from about 2 to about 90. In another embodiment, the mole ratio of the organoaluminum compound to the organosilicon compound is from about 5 to about 70. In yet another embodiment, the mole ratio of the organoaluminum compound to the organosilicon compound is from about 7 to about 35.

In one embodiment, the organosilicon compound is represented by chemical formula (IV):

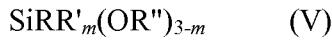


wherein each R and R' independently represent a hydrocarbon group, and n is $0 \leq n < 4$.

Specific examples of the organosilicon compound of formula (IV) include, but are not limited to trimethylmethoxysilane, trimethylethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, diisopropyldimethoxysilane, diisobutyldimethoxysilane, t-butylmethyldimethoxysilane, t-butylmethyldiethoxysilane, t-amylmethyldiethoxysilane, dicyclopentyldimethoxysilane, diphenyldimethoxysilane, phenylmethyldimethoxysilane, diphenyldiethoxysilane, bis-o-tolyldimethoxysilane, bis-m-tolyldimethoxysilane, bis-p-tolyldimethoxysilane, bis-p-toly-diethoxysilane, bisethylphenyldimethoxysilane, dicyclohexyldimethoxysilane, cyclohexylmethyldimethoxysilane, cyclohexylmethyldiethoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane,

vinyltrimethoxysilane, methyltrimethoxysilane, n-propyltriethoxysilane, decyltrimethoxysilane, decyltriethoxysilane, phenyltrimethoxysilane, gamma-chloropropyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, vinyltriethoxysilane, t-butyltriethoxysilane, n-butyltriethoxysilane, iso-butyltriethoxysilane, phenyltriethoxysilane, 5 gamma-aminopropyltriethoxysilane, cholotriethoxysilane, ethyltriisopropoxysilane, vinyltributoxysilane, cyclohexyltrimethoxysilane, cyclohexyltriethoxysilane, 2-norbornanetrimethoxysilane, 2-norbornanetriethoxysilane, 2-norbornanemethyldimethoxysilane, ethyl silicate, butyl silicate, trimethylphenoxy silane, and methyl-triallyloxysilane.

10 In another embodiment, the organosilicon compound is represented by chemical formula (V):



In the above formula (V), $0 \leq m < 3$, such as $0 \leq m \leq 2$; and R independently represents a cyclic hydrocarbon or substituted cyclic hydrocarbon group. Specific examples of the group R 15 include, but are not limited to cyclopropyl; cyclobutyl; cyclopentyl; 2-methylcyclopentyl; 3-methylcyclopentyl; 2-ethylcyclopentyl; 3-propylcyclopentyl; 3-isopropylcyclopentyl; 3-butylcyclopentyl; 3-tertiary butyl cyclopentyl; 2,2-dimethylcyclopentyl; 2,3-dimethylcyclopentyl; 2,5-dimethyl-cyclopentyl; 2,2,5-trimethylcyclopentyl; 2,3,4,5-tetramethylcyclopentyl; 2,2,5,5-tetramethylcyclopentyl; 1-cyclopentylpropyl; 1-20 methyl-1-cyclopentylethyl; cyclopentenyl; 2-cyclopentenyl; 3-cyclopentenyl; 2-methyl-1-cyclopentenyl; 2-methyl-3-cyclopentenyl; 3-methyl-3-cyclopentenyl; 2-ethyl-3-cyclopentenyl; 2,2-dimethyl-3-cyclopentenyl; 2,5-dimethyl-3-cyclopentenyl; 2,3,4,5-tetramethyl-3-cyclopentenyl; 2,2,5,5-tetramethyl-3-cyclopentenyl; 1,3-cyclopentadienyl;

2,4-cyclopentadienyl; 1,4-cyclopentadienyl; 2-methyl-1,3-cyclopentadienyl;
2-methyl-2,4-cyclopentadienyl; 3-methyl-2,4-cyclopentadienyl; 2-ethyl-2,4-cyclopentadienyl;
2,2-dimethyl-2,4-cyclopentadienyl; 2,3-dimethyl-2,4-cyclopentadienyl;
2,5-dimethyl-2,4-cyclopentadienyl; 2,3,4,5-tetramethyl-2,4-cyclopentadienyl; indenyl;
5 2-methylindenyl; 2-ethylindenyl; 2-indenyl; 1-methyl-2-indenyl; 1,3-dimethyl-2-indenyl;
indenyl; 2-methylindenyl; 2-indenyl; 1,3-dimethyl-2-indenyl; 4,5,6,7-tetrahydroindenyl;
4,5,6,7-tetrahydro-2-indenyl; 4,5,6,7-tetrahydro-1-methyl-2-indenyl;
4,5,6,7-tetrahydro-1,3-dimethyl-2-indenyl; fluorenyl groups; cyclohexyl; methylcyclohexyls;
ethylcyclohexyls; propylcyclohexyls; isopropylcyclohexyls; n-butylcyclohexyls; tertiary-butyl
10 cyclohexyls; dimethylcyclohexyls; and trimethylcyclohexyls.

In formula (V), R' and R" are identical or different and each represents a hydrocarbons. Examples of R' and R" are alkyl, cycloalkyl, aryl and aralkyl groups having 3 or more carbon atoms. Furthermore, R and R' may be bridged by an alkyl group, etc. General examples of organosilicon compounds are those of formula (V) in which R is a cyclopentyl group, R' is an alkyl group such as methyl or cyclopentyl group, and R" is an alkyl group, particularly a methyl or ethyl group.

Specific examples of the organosilicon compound of formula (V) include, but are not limited to trialkoxysilanes such as cyclopropyltrimethoxysilane, cyclobutyltrimethoxysilane, cyclopentyltrimethoxysilane, 2-methylcyclopentyltrimethoxysilane, 2,3-dimethylcyclopentyltrimethoxysilane, 2,5-dimethylcyclopentyltrimethoxysilane, cyclopentyltriethoxysilane, cyclopentenyltrimethoxysilane, 3-cyclopentenyltrimethoxysilane, 2,4-cyclopentadienyltrimethoxysilane, indenyltrimethoxysilane and fluorenyltrimethoxysilane; dialkoxy silanes, such as dicyclopentyldimethoxysilane, bis(2-methylcyclopentyl)dimethoxysilane, bis(3-tertiary

butylcyclopentyl)dimethoxysilane, bis(2,3-dimethylcyclopentyl)dimethoxysilane, bis(2,5-dimethylcyclopentyl)dimethoxysilane, dicyclopentyldiethoxysilane, dicyclobutyl-diethoxysilane, cyclopropylcyclobutyldiethoxysilane, dicyclopentenylmethoxysilane, di(3-cyclopentenyl)dimethoxysilane, bis(2,5-dimethyl-3-cyclopentenyl)dimethoxysilane, 5 di-2,4-cyclopentadienyl)dimethoxysilane, bis(2,5-dimethyl-2,4-cyclopentadienyl)-dimethoxysilane, bis(1-methyl-1-cyclopentylethyl)dimethoxysilane, cyclopentylcyclopentenyl-dimethoxysilane, cyclopentylcyclopentadienylmethoxysilane, diindenylmethoxysilane, bis(1,3-dimethyl-2-indenyl)dimethoxysilane, cyclopentadienylindenylmethoxysilane, difluorenyldimethoxysilane, cyclopentylfluorenyldimethoxysilane and indenylfluorenyl-10 dimethoxysilane; monoalkoxysilanes such as tricyclopentylmethoxysilane, tricyclopentenylmethoxysilane, tricyclopentadienylmethoxysilane, tricyclopentylethoxysilane, dicyclopentylmethylmethoxysilane, dicyclopentylethyl methoxysilane, dicyclopentyl-methylethoxysilane, cyclopentyldimethylmethoxysilane, cyclopentyldiethylmethoxysilane, cyclopentyldimethylethoxysilane, bis(2,5-dimethylcyclopentyl)cyclopentylmethoxysilane, 15 dicyclopentylcyclopentenylmethoxysilane, dicyclopentylcyclopentenadienylmethoxysilane and diindenylcyclopentylmethoxysilane; and ethylenebis-cyclopentyldimethoxysilane.

Polymerization of olefins in accordance with the present disclosure is carried out in the presence of the catalyst system described above. Generally speaking, olefins are contacted with the catalyst system described above under suitable conditions to form desired polymer products. 20 In one embodiment, preliminary polymerization described below is carried out before the main polymerization. In another embodiment, polymerization is carried out without preliminary polymerization. In yet another embodiment, the formation of copolymer is carried out using at least two polymerization zones.

In preliminary polymerization, the solid catalyst component is usually employed in combination with at least a portion of the organoaluminum compound. This may be carried out in the presence of part or the whole of the organosilicon compound (external electron donor compound). The concentration of the catalyst system used in the preliminary polymerization

5 may be much higher than that in the reaction system of the main polymerization.

In preliminary polymerization, the concentration of the solid catalyst component in the preliminary polymerization is usually from about 0.01 to about 200 millimoles, preferably from about 0.05 to about 100 millimoles, calculated as titanium atoms per liter of an inert hydrocarbon medium described below. In one embodiment, the preliminary polymerization is carried out by

10 adding an olefin and the above catalyst system ingredients to an inert hydrocarbon medium and polymerizing the olefin under mild conditions.

Specific examples of the inert hydrocarbon medium include, but are not limited to aliphatic hydrocarbons such as propane, butane, pentane, hexane, heptanes, octane, decane, dodecane and kerosene; alicyclic hydrocarbons such as cyclopentane, cyclohexane and

15 methylcyclopentane; aromatic hydrocarbons such as benzene, toluene and xylene; and mixtures thereof. In another embodiment, a liquid olefin may be used in place of part or the whole of the inert hydrocarbon medium.

The olefin used in the preliminary polymerization may be the same as, or different from, an olefin to be used in the main polymerization.

20 The reaction temperature for the preliminary polymerization is sufficient for the resulting preliminary polymer to not substantially dissolve in the inert hydrocarbon medium. In one embodiment, the temperature is from about -20 degrees Celsius to about 100 degrees Celsius. In another embodiment, the temperature is from about -10 degrees Celsius to about 80 degrees

Celsius. In yet another embodiment, the temperature is from about 0 degrees Celsius to about 40 degrees Celsius.

Optionally, a molecular-weight controlling agent, such as hydrogen, may be used in the preliminary polymerization. The molecular weight controlling agent is used in such an amount 5 that the polymer obtained by the preliminary polymerization has an intrinsic viscosity, measured in decalin at 135 degrees Celsius, of at least about 0.2 dl/g, and preferably from about 0.5 to 10 dl/g.

In one embodiment, the preliminary polymerization is desirably carried out so that from about 0.1 g to about 1,000 g of a polymer is formed per gram of the solid catalyst component of 10 the catalyst system. In another embodiment, the preliminary polymerization is desirably carried out so that from about 0.3 g to about 500 g of a polymer is formed per gram of the solid catalyst component. If the amount of the polymer formed by the preliminary polymerization is too large, the efficiency of producing the olefin polymer in the main polymerization may sometimes decrease, and when the resulting olefin polymer is molded into a film or another article, fish eyes 15 tend to occur in the molded article. The preliminary polymerization may be carried out batchwise or continuously.

After the preliminary polymerization conducted as above, or without performing any preliminary polymerization, the main polymerization of an olefin is carried out in the presence of the above-described olefin polymerization catalyst system formed from the solid catalyst 20 component, the organoaluminum compound and the organosilicon compound (external electron donor compound).

Examples of olefins that can be used in the main polymerization are alpha-olefins having 2 to 20 carbon atoms such as ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-pentene,

1-octene, 1-hexene, 3-methyl-1-pentene, 3-methyl-1-butene, 1-decene, 1-tetradecene, 1-eicosene, and vinylcyclohexane. In the process of the embodiments of present invention, these alpha-olefins may be used individually or in any combination.

In one embodiment, propylene or 1-butene is homopolymerized, or a mixed olefin 5 containing propylene or 1-butene as a main component is copolymerized. When the mixed olefin is used, the proportion of propylene or 1-butene as the main component is usually at least about 50 mole %, preferably at least about 70 mole %.

By performing the preliminary polymerization, the catalyst system in the main polymerization can be adjusted in the degree of activity. This adjustment tends to result in a 10 powdery polymer having a high bulk density. Furthermore, when the preliminary polymerization is carried out, the particles shape of the resulting polymer becomes spherical, and in the case of slurry polymerization, the slurry attains excellent characteristics while in the case of gas phase polymerization, the polymer seed bed attains excellent characteristics. Furthermore, in these embodiments, a polymer having a high stereoregularity index can be produced with a 15 high catalytic efficiency by polymerizing an alpha-olefin having at least 3 carbon atoms. Accordingly, when producing the propylene copolymer, the resulting copolymer powder or the copolymer becomes easy to handle.

In the homopolymerization of these olefins, a polyunsaturated compound such as conjugated diene or non-conjugated diene may be used as a co-monomer. Examples of co- 20 monomers include styrene, butadiene, acrylonitrile, acrylamide, alpha-methyl styrene, chlorostyrene, vinyl toluene, divinyl benzene, diallylphthalate, alkyl methacrylates and alkyl acrylates. In one embodiment, the co-monomers include thermoplastic and elastomeric monomers.

The main polymerization of an olefin is carried out usually in the gaseous or liquid phase. In one embodiment, polymerization (main polymerization) employs a catalyst system containing the solid catalyst component in an amount from about 0.001 to about 0.75 millimoles calculated as Ti atom per liter of the volume of the polymerization zone, the organoaluminum compound in 5 an amount from about 1 to about 2,000 moles per mole of titanium atoms in the solid catalyst component, and the organosilicon compound in an amount from about 0.001 to about 10 moles calculated as Si atoms in the organosilicon compound per mole of the metal atoms in the organoaluminum compound. In another embodiment, polymerization employs a catalyst system containing the solid catalyst component in an amount of from 0.005 to about 0.5 millimoles 10 calculated as Ti atom per liter of the volume of the polymerization zone, the organoaluminum compound in an amount from about 5 to about 500 moles per mole of titanium atoms in the solid catalyst component, and the organosilicon compound in an amount from about 0.01 to about 2 moles calculated as Si atoms in the organosilicon compound per mole of the metal atoms in the organoaluminum compound. In yet another embodiment, polymerization employs a catalyst 15 system containing the alkyl benzoate derivative in an amount from about 0.005 to about 1 mole calculated as Si atoms in the organosilicon compound per mole of the metal atoms in the organoaluminum compound.

When the organoaluminum compound and the organosilicon compound are used partially in the preliminary polymerization, the catalyst system subjected to the preliminary 20 polymerization is used together with the remainder of the catalyst system components. The catalyst system subjected to the preliminary polymerization may contain the preliminary polymerization product.

The use of hydrogen at the time of polymerization promotes and contributes to control of the molecular weight of the resulting polymer, and the polymer obtained may have a high melt flow rate. In this case, the stereoregularity index of the resulting polymer and the activity of the catalyst system are increased according to exemplary methods of the present invention.

5 In one embodiment, the polymerization temperature is from about 20 degrees Celsius to about 200 degrees Celsius. In another embodiment, the polymerization temperature is from about 50 degrees Celsius to about 180 degrees Celsius. In one embodiment, the polymerization pressure is typically from atmospheric pressure to about 100 kg/cm². In another embodiment, the polymerization pressure is typically from about 2 kg/cm² to about 50 kg/cm². The main 10 polymerization may be carried out batchwise, semi-continuously or continuously. The polymerization may also be carried out in two or more stages under different reaction conditions.

15 The olefin polymer so obtained may be a homopolymer, a random copolymer, a block copolymer or an impact copolymer. The impact copolymer contains an intimate mixture of a polyolefin homopolymer and a polyolefin rubber. Examples of polyolefin rubbers include ethylene propylene rubber (EPR) such as ethylene propylene methylene copolymer rubber (EPM) and ethylene propylene diene methylene terpolymer rubber (EPDM).

The olefin polymer obtained by using the catalyst system has a very small amount of an amorphous polymer component and therefore a small amount of a hydrocarbon-soluble component. Accordingly, a film molded from the resultant polymer has low surface tackiness.

20 The polyolefin obtained by the polymerization process is excellent in particle size distribution, particle diameter and bulk density, and the copolyolefin obtained has a narrow composition distribution. In an impact copolymer, excellent fluidity, low temperature resistance, and a desired balance between stiffness and elasticity can be obtained.

In one embodiment, propylene and an alpha-olefin having 2 or from about 4 to about 20 carbon atoms are copolymerized in the presence of the catalyst system described above. The catalyst system may be one subjected to the preliminary polymerization described above. In another embodiment, propylene and an ethylene rubber are formed in two reactors coupled in 5 series to form an impact polymer.

The alpha-olefin having 2 carbon atoms is ethylene, and examples of the alpha-olefin having about 4 to about 20 carbon atoms are 1-butene, 1-pentene, 4-methyl-1-pentene, 1-octene, 1-hexene, 3-methyl-1-pentene, 3-methyl-1-butene, 1-decene, vinylcyclohexane, 1-tetradecene, and the like.

10 In the main polymerization, propylene may be copolymerized with two or more such alpha-olefins. For example, it is possible to copolymerize propylene with ethylene and 1-butene. In one embodiment, propylene is copolymerized with ethylene, 1-butene or ethylene and 1-butene.

15 Block copolymerization of propylene and another alpha-olefin may be carried out in two stages. The polymerization in a first stage may be the homopolymerization of propylene or the co-polymerization of propylene with the other alpha-olefin. In one embodiment, the amount of the monomers polymerized in the first stage is from about 50 to about 95% by weight. In another embodiment, the amount of the monomers polymerized in the first stage is from about 60 to about 90% by weight. In certain embodiments, this first stage polymerization may, as 20 required, be carried out in two or more stages under the same or different polymerization conditions.

In one embodiment, the polymerization in a second stage is desirably carried out such that the mole ratio of propylene to the other alpha-olefin(s) is from about 10/90 to about 90/10.

In another embodiment, the polymerization in a second stage is desirably carried out such that the mole ratio of propylene to the other alpha-olefin(s) is from about 20/80 to about 80/20. In yet another embodiment, the polymerization in a second stage is desirably carried out such that the mole ratio of propylene to the other alpha-olefin(s) is from about 30/70 to about 70/30.

5 Producing a crystalline polymer or copolymer of another alpha-olefin may be provided in the second polymerization stage.

The propylene copolymer so obtained may be a random copolymer or the above-described block copolymer. This propylene copolymer typically contains from about 7 to about 50 mole % of units derived from the alpha-olefin having 2 or from about 4 to about 20 10 carbon atoms. In one embodiment, a propylene random copolymer contains from about 7 to about 20 mole % of units derived from the alpha-olefin having 2 or from about 4 to about 20 carbon atoms. In another embodiment, the propylene block copolymer contains from about 10 to about 50 mole % of units derived from the alpha-olefin having 2 or 4-20 carbon atoms.

In another embodiment, copolymers made with the catalyst system contain from about 15 50% to about 99% by weight poly-alpha-olefins and from about 1% to about 50% by weight co-monomers (such as thermoplastic or elastomeric monomers). In another embodiment, copolymers made with the catalyst system contain from about 75% to about 98% by weight poly-alpha-olefins and from about 2% to about 25% by weight co-monomers.

It should be understood that where there is no reference to the polyunsaturated compound 20 that can be used, the method of polymerization, the amount of the catalyst system and the polymerization conditions, the same description as the above embodiment are applicable.

The catalysts/methods of the present disclosure can in some instances lead to the production of poly-alpha-olefins having xylene soluble (XS) from about 0.5% to about 10%. In

another embodiment, poly-alpha-olefins having xylene soluble (XS) from about 1.5% to about 8% are produced. XS refers to the percent of solid polymer that dissolves into xylene. A low XS % value generally corresponds to a highly isotactic polymer (i.e. higher crystallinity), whereas a high XS % value generally corresponds to a low isotactic polymer.

5 In one embodiment, the catalyst efficiency (measured as kilogram of polymer produced per gram of catalyst) of the catalyst system of embodiments of the present invention is at least about 30. In another embodiment, the catalyst efficiency of the catalyst system of embodiments of the present invention is at least about 60.

The catalysts/methods can in some instances lead to the production of poly-alpha-olefins
10 having melt flow indexes (MFI) from about 0.1 to about 100. The MFI is measured according to ASTM standard D1238. In another embodiment, poly-alpha-olefins having an MFI from about 5 to about 30 are produced. In one embodiment, an impact polypropylene-ethylenepropylene rubber product has an MFI from about 4 to about 10. In another embodiment, an impact polypropylene-ethylenepropylene rubber product has an MFI from about 5 to about 9. In some
15 instances a relatively high MFI indicates relatively high catalyst efficiency is obtainable.

The catalysts/methods can in some instances lead to the production of poly-alpha-olefins having bulk densities (BD) of at least about 0.3 cc/g. In another embodiment, poly-alpha-olefins having a BD of at least about 0.4 cc/g are produced.

In one embodiment, an impact polypropylene-ethylenepropylene rubber product having a
20 BD of at least about 0.3 cc/g is produced. In another embodiment, an impact polypropylene-ethylenepropylene rubber product having a BD of at least about 0.4 cc/g is produced.

The catalysts/methods lead to the production of poly-alpha-olefins having a relatively narrow molecular weight distribution. Polydispersive Index (PI) is strictly connected with the molecular weight distribution of the polymer. PI is calculated as the weight average molecular weight divided by the number average molecular weight, $PI=M_w/M_n$. In one embodiment, the PI 5 of a polypropylene polymer made with the catalyst system is from about 2 to about 12. In another embodiment, the PI of a polypropylene polymer made with the catalyst system is from about 5 to about 11.

Embodiments of the present disclosure can lead to the production of a propylene block copolymer and impact copolymers including polypropylene based impact copolymer having one 10 or more excellent melt-flowability, moldability desirable balance between rigidity and elasticity, good stereospecific control, good control over polymer particle size, shape, size distribution, and molecular weight distribution, and impact strength with a high catalytic efficiency and/or good operability. Employing the catalyst systems containing the solid catalyst component according to embodiments of the present invention yields catalysts simultaneously having high catalytic 15 efficiency, and one or more of excellent melt-flowability, extrudability, moldability, rigidity-elasticity and impact strength.

Examples of systems for polymerizing olefins are now described. Referring to FIG. 1, a high level schematic diagram of a system **10** for polymerizing olefins is shown. Inlet **12** is used to introduce into a reactor **14** catalyst system components, olefins, optional co-monomers, 20 hydrogen gas, fluid media, pH adjusters, surfactants, and any other additives. Although only one inlet is shown, many often are employed. Reactor **14** is any suitable vehicle that can polymerize olefins. Examples of reactor **14** include a single reactor, a series of two or more reactors, slurry reactors, fixed bed reactors, gas phase reactors, fluidized gas reactors, loop reactors, multizone

circulating reactors, and the like. Once polymerization is complete, or as polyolefins are produced, the polymer product is removed from the reactor **14** via outlet **16** which leads to a collector **18**. Collector **18** may include downstream processing, such as heating, extrusion, molding, and the like.

5 Referring to FIG. 2, a schematic diagram of a multizone circulating reactor **20** that can be employed as the reactor **14** in FIG. 1 or the reactor **44** in FIG. 3 for making polyolefins is shown. The multizone circulating reactor **20** substitutes a series of separate reactors with a single reactor loop that permits different gas phase polymerization conditions in two sides due to use of a liquid barrier. In the multi-zone circulating reactor **20**, a first zone starts out rich in olefin monomers, 10 and optionally one or more co-monomers. A second zone is rich in hydrogen gas, and a high velocity gas flow divides the growing resin particles out loosely. The two zones produce resins of different molecular weights and/or monomer compositions. Polymer granules grow as they circulate around the loop, building up alternating layers of each polymer fraction in an onion like fashion. Each polymer particle constitutes an intimate combination of both polymer fractions.

15 In operation, the polymer particles pass up through the fluidizing gas in an ascending side **24** of the loop and come down through the liquid monomer on a descending side **26**. The same or different monomers (and again optionally one or more co-monomers) can be added in the two reactor legs. The reactor uses the catalyst system described above.

In the liquid/gas separation zone **30**, hydrogen gas is removed to cool and recirculate. 20 Polymer granules are then packed into the top of the descending side **26**, where they then descend. Monomers are introduced as liquids in this section. Conditions in the top of the descending side **26** can be varied with different combinations and/or proportions of monomers in successive passes.

Referring to FIG. 3, a high level schematic diagram of another system 40 for polymerizing olefins is shown. This system is ideally suited to make impact polymers. A reactor 44, such as a single reactor, a series of reactors, or a multizone circulating reactor is paired with a gas phase or a fluidized bed reactor 48 downstream containing the catalyst systems described above to make impact copolymers with desirable impact to stiffness balance or greater softness than made with conventional catalyst systems. Inlet 42 is used to introduce into the reactor 44 catalyst system components, olefins, optional co-monomers, hydrogen gas, fluid media, pH adjusters, surfactants, and any other additives. Although only one inlet is shown, many often are employed. Through transfer means 46 the polyolefin made in the first reactor 44 is sent to a second reactor 48. Feed 50 is used to introduce catalyst system components, olefins, optional co-monomers, fluid media, and any other additives. The second reactor 48 may or may not contain catalyst system components. Again, although only one inlet is shown, many often are employed. Once the second polymerization is complete, or as impact copolymers are produced, the polymer product is removed from the second reactor 48 via outlet 52 which leads to a collector 54. Collector 54 may include downstream processing, such as heating, extrusion, molding, and the like. At least one of the first reactor 44 and the second reactor 48 contains catalyst systems in accordance with the invention.

When making an impact copolymer, polypropylene can be formed in the first reactor while an ethylene propylene rubber can be formed in the second reactor. In this polymerization, the ethylene propylene rubber in the second reactor is formed with the matrix (and particularly within the pores) of the polypropylene formed in the first reactor. Consequently, an intimate mixture of an impact copolymer is formed, wherein the polymer product appears as a single

polymer product. Such an intimate mixture cannot be made by simply mixing a polypropylene product with an ethylene propylene rubber product.

Although not shown in any of the figures, the systems and reactors can be controlled, optionally with feedback based on continuous or intermittent testing, using a processor equipped 5 with an optional memory and controllers. For example, a processor may be connected to one or more of the reactors, inlets, outlets, testing/measuring systems coupled with the reactors, and the like to monitor and/or control the polymerization process, based on preset data concerning the reactions, and/or based on testing/measuring data generated during a reaction. The controller may control valves, flow rates, the amounts of materials entering the systems, the conditions 10 (temperature, reaction time, pH, etc.) of the reactions, and the like, as instructed by the processor. The processor may contain or be coupled to a memory that contains data concerning various aspects of the polymerization process.

With respect to any figure or numerical range for a given characteristic, a figure or a parameter from one range may be combined with another figure or a parameter from a different 15 range for the same characteristic to generate a numerical range.

Other than in the operating examples, or where otherwise indicated, all numbers, values and/or expressions referring to quantities of ingredients, reaction conditions, etc., used in the specification and claims are to be understood as modified in all instances by the term “about.”

The following examples illustrate embodiments of the present disclosure. Unless 20 otherwise indicated in the following examples and elsewhere in the specification and claims, all parts and percentages are by weight, all temperatures are in degrees Celsius, and pressure is at or near atmospheric pressure.

Example 1

3.3 g MgCl₂, 0.8 g phthalic anhydride, 50.92 g toluene, 6.41 g epichlorohydrin, and 6.70 g tributylphosphate were added into a 250 ml Buchi reactor under N₂. The mixture was heated for two hours while agitating at 400 rpm at 60°C. The reaction mixture was then cooled to -30 °C and 37.75 ml of TiCl₄ was added slowly while maintaining the reactor temperature 5 below -26 °C. After the addition, the agitation rate was reduced to 200 rpm and the temperature was ramped from -26 °C to 0 °C in one hour then 0°C to 85 °C in one hour.

The mixture was held at 85 °C for 30 minute, then 0.6 g of naphthalene-1,8-diyl dibenzoate and 0.6 g of 3,3-bis(methoxymethyl)-2,6-dimethylheptane were added. The mixture was stirred at 105 °C for two hours, then filtered. After filtration, the mixture was washed twice 10 with 65 ml toluene and left over night in toluene under N₂.

After filtering off the toluene, 66.25 ml of 10 vol% TiCl₄ in toluene was added to the mixture, then the mixture was heated to and held at 105 °C with 400 rpm agitation for one hour. The solids were filtered, then re-suspended in 66.25 ml of 10 vol% TiCl₄ in toluene. The mixture was held at 110 °C for one hour, after which, the solids were once again filtered. The 15 final catalyst was washed four times with 65 ml of hexane then discharged from the reactor in hexane.

Propylene Polymerization was performed in a one gallon reactor. The reactor was purged at 100 °C under nitrogen for one hour. At room temperature, 1.5 ml of 25 wt% TEAl (Aluminium Triethyl) in heptane was added into the reactor. Then 0.94 ml of 0.0768 M solution 20 of cyclohexyl methyl dimethoxy silane was added to the reactor, followed by 7.0 mg catalyst as a 1 wt% hexane slurry. The reactor was charged with 4 standard liter H₂ followed by 1300 g propylene. The reactor was heated to and then held at 70°C for one hour. At the end of the hold, the reactor was vented and the polymer was recovered.

Yield: 464 g polypropylene. Catalyst activity: 66.3 kg/g; xylene solubles: 0.88%;
MFR: 0.9 dg/min.

Example 2

5 The catalyst in Example 1 was tested under the same conditions, except 0.63 ml of 0.0768 M solution of cyclohexyl methyl dimethoxy silane and 6.0 mg catalyst were added into the polymerization reactor.

Yield: 334 g polypropylene. Catalyst activity: 66.8 kg/g. Xylene solubles: 0.90%.
MFR: 0.7 dg/min.

10

Example 3

The catalyst in Example 2 was tested under the same conditions, except no cyclohexyl methyl dimethoxy silane was added in the mother liquor addition stage.

Yield: 405 g polypropylene. Catalyst activity: 67.5 kg/g. Xylene solubles: 1.17%.
15 MFR: 0.8 dg/min.

Example 4

The catalyst was synthesized under same conditions as Example 1, except 0.7 g of naphthalene-1,8-diyl dibenzoate and 0.7 g of 3,3-bis(methoxymethyl)-2,6-dimethylheptane was 20 added in the mother liquor addition stage.

Propylene polymerization was the same as in example 1. Yield: 447 g polypropylene.
Catalyst activity: 63.9 kg/g. Xylene solubles: 0.92%. MFR: 1.0 dg/min.

Example 5

The catalyst in Example 4 was tested under the same conditions, except 0.63 ml of 0.0768 M solution of cyclohexyl methyl dimethoxy silane and 6.0 mg catalyst were added in the polymerization reactor.

5 Yield: 417 g polypropylene. Catalyst activity: 69.5 kg/g. Xylene solubles: 0.92%.
MFR: 0.7 dg/min.

Example 6

The catalyst in Example 4 was tested under the same conditions, except no cyclohexyl
10 methyl dimethoxy silane was added in the mother liquor addition stage.

Yield: 436 g polypropylene. Catalyst activity: 72.7 kg/g. Xylene solubles: 1.48%.
MFR: 1.0 dg/min.

Example 7

15 The catalyst was synthesized under same conditions as Example 1, except 0.4 g of naphthalene-1,8-diyl dibenzoate and 0.4 g of 3,3-bis(methoxymethyl)-2,6-dimethylheptane was added in the mother liquor addition stage.

Propylene polymerization was the same as in Example 1. Yield: 429 g polypropylene.
Catalyst activity: 61.3 kg/g. Xylene solubles: 1.26%. MFR: 0.5 dg/min.

20

Example 8

The catalyst in Example 7 was tested under the same conditions, except 0.73 ml of 0.0768 M solution of cyclohexyl methyl dimethoxy silane and 6.0 mg catalyst were added in the polymerization reactor.

Yield: 427 g polypropylene. Catalyst activity: 71.2 kg/g. Xylene solubles: 1.30%.

5 MFR: 0.8 dg/min.

Example 9

The catalyst in Example 7 was tested under the same conditions, except no cyclohexyl methyl dimethoxy silane was added in the mother liquor addition stage.

10 Yield: 450 g polypropylene. Catalyst activity: 75.0 kg/g. Xylene solubles: 2.20%.

MFR: 1.4 dg/min.

Example 10

The catalyst was synthesized under same conditions as Example 1, except 0.5 g of 15 naphthalene-1,8-diyl dibenzoate and 0.5 g of 3,3-bis(methoxymethyl)-2,6-dimethylheptane was added in the mother liquor addition stage.

Propylene polymerization was the same as in Example 1. Yield: 466 g polypropylene.

Catalyst activity: 66.6 kg/g. Xylene solubles: 1.10%. MFR: 0.6 dg/min.

20

Example 11

The catalyst in Example 10 was tested under the same conditions except 0.70 ml of 0.0768 M solution of cyclohexyl methyl dimethoxy silane and 6.0 mg catalyst were added in the polymerization reactor.

Yield: 423 g polypropylene. Catalyst activity: 70.5 kg/g. Xylene solubles: 2.20%.

MFR: 1.4 dg/min.

Example 12

5 The catalyst in Example 10 was tested under the same conditions, except no cyclohexyl methyl dimethoxy silane was added in the mother liquor addition stage.

Yield: 438 g polypropylene. Catalyst activity: 73.0 kg/g. Xylene solubles: 2.00%.

MFR: 1.3 dg/min.

10

Example 13

The catalyst was synthesized under same conditions as Example 1, except 0.3 g of naphthalene-1,8-diyl dibenzoate and 0.5 g of 3,3-bis(methoxymethyl)-2,6-dimethylheptane was added in the mother liquor addition stage.

Propylene polymerization was the same as in Example 1. Yield: 448 g polypropylene.

15 Catalyst activity: 64.1 kg/g. Xylene solubles: 1.43%. MFR: 1.1 dg/min.

Example 14

The catalyst was synthesized under same conditions as Example 1, except 0.5 g of naphthalene-1,8-diyl dibenzoate and 0.3 g of 3,3-bis(methoxymethyl)-2,6-dimethylheptane was added in the mother liquor addition stage.

Propylene polymerization was the same as in Example 1. Yield: 459 g polypropylene.

Catalyst activity: 65.6 kg/g. Xylene solubles: 1.34%. MFR: 1.1 dg/min.

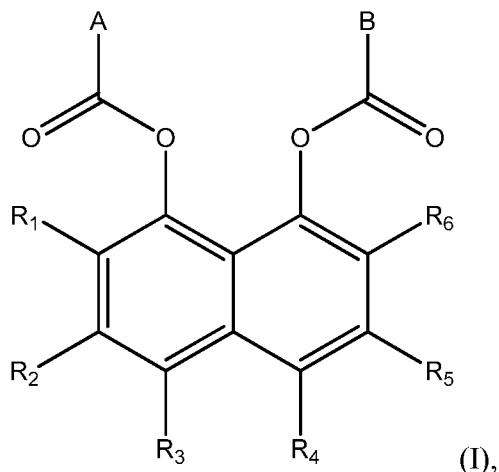
It is, of course, not possible to describe every conceivable combination of the components or methodologies for purpose of describing the disclosed information, but one of ordinary skill in the art can recognize that many further combinations and permutations of the disclosed information are possible. Accordingly, the disclosed information is intended to

5 embrace all such alternations, modifications and variations that fall within the spirit and scope of the appended claims. Furthermore, to the extent that the term “includes,” “has,” “involve,” or variants thereof is used in either the detailed description or the claims, such term is intended to be inclusive in a manner similar to the term “comprising” as “comprising” is interpreted when employed as a transitional word in a claim.

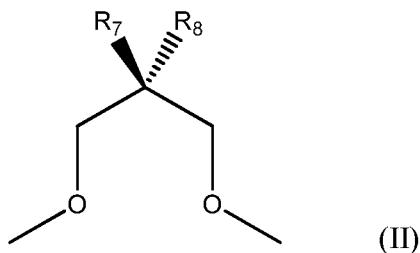
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CLAIMS

1. A solid catalyst component for use in olefinic polymerization, comprising:
titanium,
magnesium,
halogen, and
a combination of internal electron donor compounds, wherein said combination of internal electron donor compounds comprises at least one 1,8-naphthyl diester compound represented by chemical formula (I):



and at least one 3,3-bis(methoxymethyl) alkane compound represented by chemical formula (II):



wherein

R₁-R₆ are each independently hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals;

A and B, which are identical or different, are substituted or unsubstituted hydrocarbyl radicals having 3 to 20 carbon atoms; and

R₇ and R₈ which are identical or different, C₁-C₂₀ linear or branched alkyl, C₅-C₂₀ alkyl-cycloalkyl, or C₅-C₂₀ cycloalkyl-alkyl radicals.

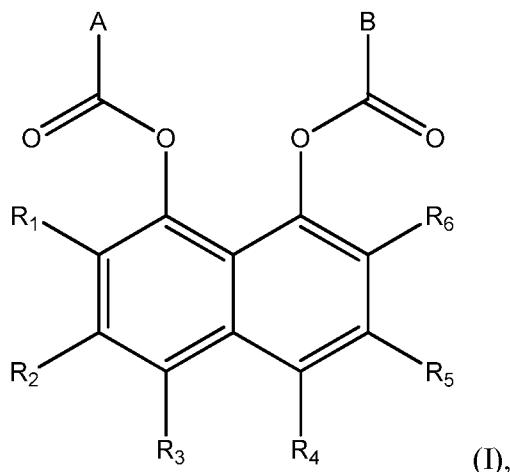
2. The solid catalyst component according to claim 1 comprising a titanium compound having at least one titanium-halogen bond and the combination of internal electron donor compounds supported on a magnesium halide crystal lattice.

3. The solid catalyst component according to claim 1 comprising a titanium compound having at least one titanium-halogen bond and the combination of internal electron donor compounds supported on a magnesium dichloride crystal lattice.

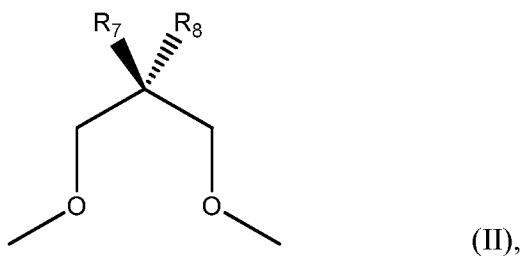
4. The solid catalyst component according to claim 2 or 3, wherein the titanium compound is TiCl₄ or TiCl₃.

5. A solid catalyst component for use in olefinic polymerization, comprising:
a reaction product of a titanium compound,

a magnesium compound, and
 a combination of internal electron donor compounds,
 wherein said combination of internal electron donor compounds comprises at least one
 1,8-naphthyl diester compound represented by chemical formula (I):



and at least one 3,3-bis(methoxymethyl) alkane compound represented by chemical formula (II):



wherein

R₁-R₆ are each independently hydrogen, halogen, C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, C₅-C₂₀ alkyl-cycloalkyl, phenyl, C₇-C₁₀ alkylaryl, or C₇-C₁₈ arylalkyl radicals;

A and B, which are identical or different, are substituted or unsubstituted hydrocarbyl radicals having 3 to 20 carbon atoms; and

R₇ and R₈ which are identical or different, C₁-C₂₀ linear or branched alkyl, C₅-C₂₀ alkyl-cycloalkyl, or C₅-C₂₀ cycloalkyl-alkyl radicals.

6. The solid catalyst component according to claim 1 or 5, wherein said 1,8-naphthyl diester compound of the formula (I) is selected from the group consisting of naphthalene-8-diyl dicyclohexanecarboxylate, naphthalene-1,8-diyl di-2-methylcyclohexanecarboxylate, naphthalene-1,8-diyl di-3-methylcyclohexanecarboxylate, naphthalene-1,8-diyl di-4-methylcyclohexanecarboxylate, naphthalene-1,8-diyl dicyclohex-1-enecarboxylate, naphthalene-1,8-diyl dicyclohex-2-enecarboxylate, naphthalene-1,8-diyl dicyclohex-3-enecarboxylate, 8-(cyclohexanecarbonyloxy)naphthalene-1-yl benzoate, 8-(2-methylcyclohexanecarbonyloxy)naphthalene-1-yl benzoate, 8-(3-methylcyclohexanecarbonyloxy)naphthalene-1-yl benzoate, 8-(4-methylcyclohexanecarbonyloxy)naphthalene-1-yl benzoate, 8-(2-methylcyclohexanecarbonyloxy)naphthalene-1-yl 2-methylbenzoate, 8-(3-methylcyclohexanecarbonyloxy)naphthalene-1-yl 2-methylbenzoate, 8-(4-methylcyclohexanecarbonyloxy)naphthalene-1-yl 2-methylbenzoate, 8-(2-methylcyclohexanecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,

8-(3-methyl cyclohexanecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(4-methylcyclohexanecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(2-methylcyclohexanecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(3-methylcyclohexanecarbonyloxy)naphthalene-1-yl 4-methylbenzoate, and
8-(4-methylcyclohexanecarbonyloxy)naphthalene-1-yl 4-methylbenzoate.

7. The solid catalyst component according to claim 1 or 5, wherein the 1,8-naphthyl diester compound of the formula (I) is selected from the group consisting of
8-(cyclohex-1-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(cyclohex-2-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(cyclohex-3-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(cyclohex-1-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(cyclohex-2-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(cyclohex-3-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(cyclohex-1-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(cyclohex-2-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(cyclohex-3-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(cyclohex-1-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(cyclohex-2-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(cyclohex-3-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(2-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(2-methyl cyclohex-2-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(2-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl benzoate,

8-(2-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(2-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(2-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(2-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(2-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(2-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(2-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(2-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(2-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(3-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(3-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(3-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(3-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(3-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(3-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(3-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(3-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(3-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(3-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 4-methyl benzoate,
8-(3-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(3-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(4-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl benzoate,

8-(4-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl benzoate,
8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(4-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 2-methylbenzoate,
8-(4-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 2-methyl benzoate,
8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(4-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 3-methyl benzoate,
8-(4-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 3-methylbenzoate,
8-(4-methylcyclohex-1-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate,
8-(4-methylcyclohex-2-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate, and
8-(4-methylcyclohex-3-enecarbonyloxy)naphthalene-1-yl 4-methylbenzoate.

8. The solid catalyst component according to claim 1 or 5, wherein at least one of R₇ and R₈ is C₁-C₂₀ linear or branched alkyl radicals.

9. The solid catalyst component according to claim 1 or 5, wherein at least one of R₇ and R₈ is C₁-C₂₀ linear or branched alkyl, C₅-C₁₀ cycloalkyl-alkyl, or C₅-C₂₀ alkyl-cycloalkyl radicals.

10. The solid catalyst component according to claim 1 or 5, wherein the at least one 3,3-bis(methoxymethyl) alkane compound represented by chemical formula (II) is selected from the group consisting of

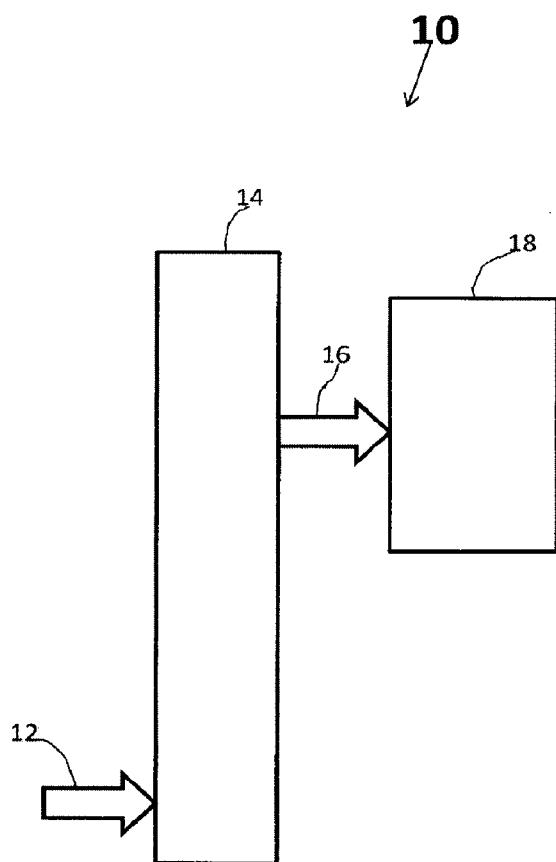
1,3-dimethoxy-2,2-dimethylpropane;
1-methoxy-2-(methoxymethyl)-2-methylbutane;
1-methoxy-2-(methoxymethyl)-2-methylpentane;

1-methoxy-2-(methoxymethyl)-2-methylhexane;
1-methoxy-2-(methoxymethyl)-2-methylheptane;
1-methoxy-2-(methoxymethyl)-2-methyloctane;
1-methoxy-2-(methoxymethyl)-2-methylnonane;
1-methoxy-2-(methoxymethyl)-2-methyldecane;
1-methoxy-2-(methoxymethyl)-2-methylundecane;
1-methoxy-2-(methoxymethyl)-2-methyldodecane;
1-methoxy-2-(methoxymethyl)-2-methyltetradecane;
1-methoxy-2-(methoxymethyl)-2-methylhexadecane;
1-methoxy-2-(methoxymethyl)-2-methyloctadecane;
1-methoxy-2-(methoxymethyl)-2-methylicosane;
1-methoxy-2-(methoxymethyl)-2-methyldocosane;
1-methoxy-2-(methoxymethyl)-2,3-dimethylbutane;
1-methoxy-2-(methoxymethyl)-2,4-dimethylpentane;
1-methoxy-2-(methoxymethyl)-2,5-dimethylhexane;
1-methoxy-2-(methoxymethyl)-2,6-dimethylheptane;
1-methoxy-2-(methoxymethyl)-2,7-dimethyloctane;
1-methoxy-2-(methoxymethyl)-2,8-dimethylnonane;
1-methoxy-2-(methoxymethyl)-2,9-dimethyldecane;
1-methoxy-2-(methoxymethyl)-2,10-dimethylundecane;
1-methoxy-2-(methoxymethyl)-2,11-dimethyldodecane;
1-methoxy-2-(methoxymethyl)-2,13-dimethyltetradecane;
1-methoxy-2-(methoxymethyl)-2,15-dimethylhexadecane;

1-methoxy-2-(methoxymethyl)-2,17-dimethyloctadecane;
1-methoxy-2-(methoxymethyl)-2,19-dimethylicosane;
1-methoxy-2-(methoxymethyl)-2,21-dimethyldocosane;
3,3-bis(methoxymethyl)-2,4-dimethylpentane;
3,3-bis(methoxymethyl)-2,5-dimethylhexane;
3,3-bis(methoxymethyl)-2,6-dimethylheptane;
3,3-bis(methoxymethyl)-2,7-dimethyloctane;
5,5-bis(methoxymethyl)-2,9-dimethyldecane;
4,4-bis(methoxymethyl)-2,6-dimethylheptane;
4,4-bis(methoxymethyl)-2,7-dimethyloctane;
4,4-bis(methoxymethyl)-2,8-dimethylnonane;
5,5-bis(methoxymethyl)-2,8-dimethylnonane;
6,6-bis(methoxymethyl)-2,10-dimethylundecane;
3,3-bis(methoxymethyl)-2-methylpentane;
4,4-bis(methoxymethyl)-2-methylhexane;
5,5-bis(methoxymethyl)-2-methylheptane;
6,6-bis(methoxymethyl)-2-methyloctane;
6,6-bis(methoxymethyl)-2-methyldecane;
4,4-bis(methoxymethyl)-2-methylheptane;
5,5-bis(methoxymethyl)-2-methyloctane;
6,6-bis(methoxymethyl)-2-methylnonane;
5,5-bis(methoxymethyl)-2-methylnonane;
6,6-bis(methoxymethyl)-2-methylundecane;

3,3-bis(methoxymethyl)pentane;
3,3-bis(methoxymethyl)hexane;
3,3-bis(methoxymethyl)heptane;
3,3-bis(methoxymethyl)octane;
5,5-bis(methoxymethyl)decane;
4,4-bis(methoxymethyl)heptane;
4,4-bis(methoxymethyl)octane;
4,4-bis(methoxymethyl)nonane;
5,5-bis(methoxymethyl)nonane;
6,6-bis(methoxymethyl)undecane;
(1,3-dimethoxy-2-methylpropan-2-yl)cyclohexane;
(3-methoxy-2-(methoxymethyl)-2-methylpropyl)cyclohexane
1-(3-methoxy-2-(methoxymethyl)-2-methylpropyl)-4-methylcyclohexane;
1-(1,3-dimethoxy-2-methylpropan-2-yl)-4-methylcyclohexane;
(1,3-dimethoxy-2-methylpropan-2-yl)cyclopentane; and
1-(1,3-dimethoxy-2-methylpropan-2-yl)-3-methylcyclopentane.

1 of 3

**FIG. 1**

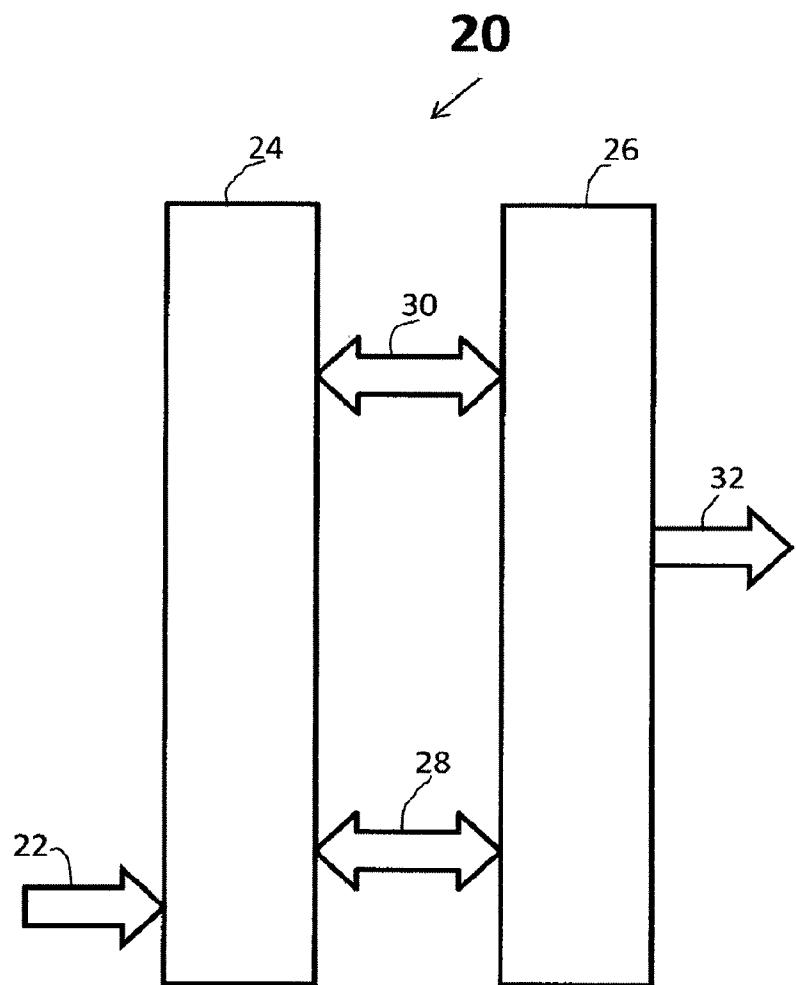


FIG. 2

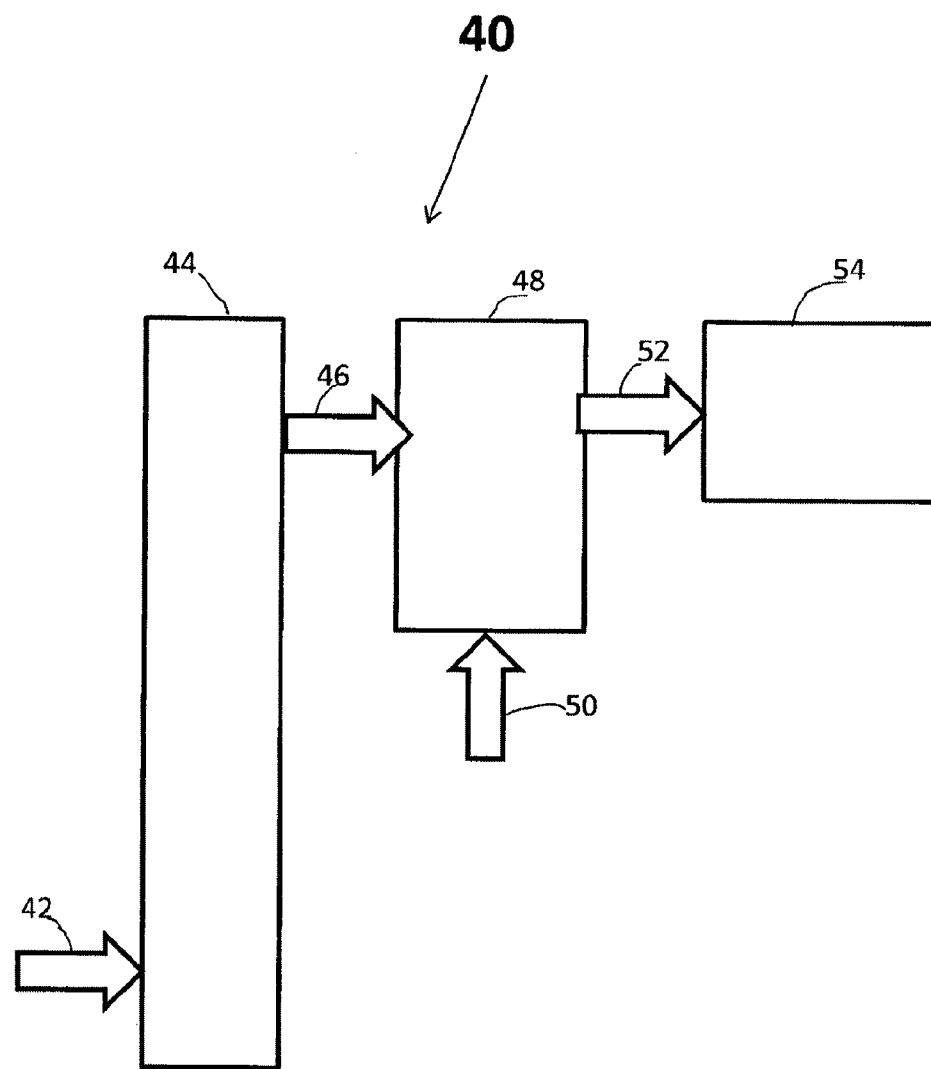


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/019961

A. CLASSIFICATION OF SUBJECT MATTER

C08F 4/64(2006.01)i, C08F 4/654(2006.01)i, C08F 10/00(2006.01)i, C08F 2/00(2006.01)i

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 4/64; C08F 4/16; B01J 31/02; C08F 4/76; B01J 31/14; C08F 4/44; B01J 31/38; B01J 31/04; C08F 4/654; C08F 10/00; C08F 2/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: solid catalyst, titanium, magnesium, halogen, internal electron donor, 1,8-naphthyl diester, 3,3-bis(methoxymethyl)alkane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2011-0213106 A1 (CHANG, M.) 01 September 2011 See abstract; paragraphs [0012]–[0024]; and claims 1–9.	1–10
Y	US 2011-0040051 A1 (XIE, L. et al.) 17 February 2011 See abstract; paragraphs [0064], [0066]; and claims 1, 14.	1–10
A	US 2012-0116031 A1 (CHANG, M.) 10 May 2012 See abstract; paragraphs [0049]–[0060]; and claims 1, 7–23.	1–10
A	US 6300273 B1 (SACCHETTI, M. et al.) 09 October 2001 See abstract; column 3, lines 12–61; and claims 1–16.	1–10
A	US 2002-0137860 A1 (COLLINA, G. et al.) 26 September 2002 See abstract; paragraphs [0008], [0009], [0016]; and claim 1.	1–10

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 19 May 2014 (19.05.2014)	Date of mailing of the international search report 19 May 2014 (19.05.2014)
Name and mailing address of the ISA/KR International Application Division Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea Facsimile No. +82-42-472-7140	Authorized officer KIM, Eun Hee Telephone No. +82-42-481-5543



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/019961

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/019961

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		DE 69720338 T2	12/02/2004
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