

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

(19) World Intellectual Property Organization

International Bureau



(10) International Publication Number

WO 2017/120310 A1

(43) International Publication Date

13 July 2017 (13.07.2017)

(51) International Patent Classification:

B01J 31/12 (2006.01) *C07C 2/30* (2006.01)
B01J 31/14 (2006.01) *C07C 11/08* (2006.01)
B01J 31/02 (2006.01)

(74) Agents: INGLE, Cory J. et al.; Dinsmore & Shohl LLP, One South Main Street, Suite 1300, Dayton, Ohio 45402 (US).

(21) International Application Number:

PCT/US2017/012299

(22) International Filing Date:

5 January 2017 (05.01.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/275,932 7 January 2016 (07.01.2016) US

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, 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, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, 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.

(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, ST, 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))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))



WO 2017/120310 A1

(54) Title: ANTIFOULING OLIGOMERIZATION CATALYST SYSTEMS

(57) Abstract: Described is a catalyst system that reduces polymeric fouling in olefin oligomerisation, in particular dimerization of ethylene to 1-butene, and comprises at least one titanate compound, at least one aluminum compound, and at least one antifouling agent. The antifouling agent comprises a structure comprising a central aluminum atom bound to an R1 group, bound to an R2 group, and bound to an R3 group. One or more of the chemical groups R1, R2, and R3 are antifouling groups comprising the structure $-O((CH_2)_nO)_mR4$, where n is an integer from 1 to 20, m is an integer from 1 to 100, and R4 is a hydrocarbyl group. The chemical groups R1, R2, or R3 that do not comprise the antifouling group, if any, are hydrocarbyl groups.

ANTIFOULING OLIGOMERIZATION CATALYST SYSTEMS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/275,932 filed January 7, 2016, and entitled “ANTIFOULING OLIGOMERIZATION CATALYST SYSTEMS,” which is incorporated into this disclosure by reference in its entirety.

BACKGROUND

Field

[0002] Embodiments of the present disclosure generally relate to catalyst systems used in ethylene oligomerization and, more specifically, relate to antifouling catalyst systems used in ethylene oligomerization which reduce undesired polymerization.

Technical Background

[0003] 1-butene and 1-hexene are important petrochemicals, especially for the productions of polyethylene. The reaction of ethylene and other alpha-olefins, especially 1-butene and 1-hexene, forms various grades of linear low density polyethylene (LLDPE), a useful commercial polymer. A source of 1-butene is the butene fraction from the effluent of a hydrocarbon cracker, such as a steam cracker or fluidized catalytic cracker. However, the process for recovering 1-butene from such an effluent requires several difficult process steps that may make the process undesirable.

[0004] Several commercial processes selectively oligomerize ethylene into alpha olefins such as 1-butene and 1-hexene. A commercially successful dimerization process is the Alphabutol™ Process, developed by the Institute Francais du Petrole (IFP), described in A. Forestiere, et al., “Oligomerization of Monoolefins by Homogenous Catalysts”, Oil & Science and Technology—Review de l’Institute Francais du Petrole, pages 663-664 (Volume 64, Number 6, November 2009). This process uses a bubble-point reactor that contains 1-butene as a process fluid to oligomerize ethylene selectively into 1-butene.

[0005] There is a known problem with oligomerization systems: polymer formation. Long residence times and poor heat removal from the highly exothermic reactions lead to the

formation of polyethylene-based residues. A side effect of chronic fouling is increasingly frequent process shutdowns and higher maintenance costs for removing adhered polymer residues. Polymer residues may build layer upon layer and eventually close off openings and ports in locations with fluid flow. Additionally, a polymer coating along the wall of a reactor may act as an insulator, which may negatively affect heat transfer to the reactor system. Polymer can also collect debris that can be catalytically active or that can poison the reaction process.

[0006] An especially troublesome issue is the formation of “hot spots”. A hot spot is an area where external cooling is ineffective and catalyst activity is high. It represents a loss of process control. A hot spot can be an area of collected polymer that includes catalytically active material that fosters side-reactions, including polymerization. If left unchecked, the hot spot can eventually lead to a process shutdown due to the loss of cooling capacity, a runaway polymerization reaction, or both.

SUMMARY

[0007] There is a continual need for effective methods to prevent polymeric fouling on reactor system walls and tubes while maintaining the desired oligomerization rate and selectivity to form reaction product.

[0008] According to one embodiment, a catalyst system that reduces polymeric fouling may comprise at least one titanate compound, at least one aluminum compound, and at least one antifouling agent or a derivative thereof. The antifouling agent may comprise a structure comprising a central aluminum molecule bound to an R1 group, bound to an R2 group, and bound to an R3 group. One or more of the chemical groups R1, R2, and R3 may be antifouling groups comprising the structure $-\text{O}((\text{CH}_2)_n\text{O})_m\text{R}4$, where n is an integer from 1 to 20, m is an integer from 1 to 100, and R4 is a hydrocarbyl group. The chemical groups R1, R2, or R3 that do not comprise the antifouling group, if any, may be hydrocarbyl groups.

[0009] According to another embodiment, 1-butene may be produced by a process comprising contacting ethylene with a catalyst system to oligomerize the ethylene to form 1-butene. The catalyst system may comprise at least one titanate compound, at least one aluminum compound, and at least one antifouling agent or a derivative thereof. The antifouling agent may comprise a structure comprising a central aluminum molecule bound to an R1 group,

bound to an R2 group, and bound to an R3 group. One or more of the chemical groups R1, R2, and R3 may be antifouling groups comprising the structure $-\text{O}((\text{CH}_2)_n\text{O})_m\text{R4}$, where n is an integer from 1 to 20, m is an integer from 1 to 100, and R4 is a hydrocarbyl group. The chemical groups R1, R2, or R3 that do not comprise the antifouling group, if any, may be hydrocarbyl groups.

[0010] Additional features and advantages of the embodiments described herein will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the embodiments described, including the detailed description which subsequently follows, and the claims.

DETAILED DESCRIPTION

[0011] One or more embodiments of the present disclosure are directed to catalyst systems which may be utilized in promoting ethylene oligomerization, such as the dimerization of ethylene to form 1-butene, while reducing reactor fouling caused by undesired polymerization. These catalyst systems are sometimes referred to in this disclosure as “antifouling ethylene oligomerization catalyst systems” or “antifouling catalyst systems”. The antifouling catalyst systems described may comprise at least one titanate compound, at least one aluminum compound, and at least one antifouling agent or dimer thereof. The antifouling catalyst systems may further comprise one or more ether compounds. The antifouling catalyst systems may be used to selectively oligomerize ethylene to produce 1-butene, while reducing undesirable polymerization, sometimes referred to in this disclosure as “fouling”. For example, reactor fouling may occur due to the formation of solid polyethylene-based residues which may reduce fluid flow and fully block or at least partially block fluids in a reactor system from flowing at a desired rate. It should be understood that the “antifouling ethylene oligomerization catalyst systems” or “antifouling catalyst systems” described may not completely eliminate fouling during a reaction. However, these catalyst systems reduce fouling as compared with catalyst systems which do not include an antifouling agent as described in the present disclosure. Also, it should be understood that while the catalyst systems of the present disclosure may be useful in ethylene oligomerization reactions, such as ethylene dimerization to form 1-butene, they may also be useful for the catalysis of other chemical reaction, and the antifouling catalyst systems

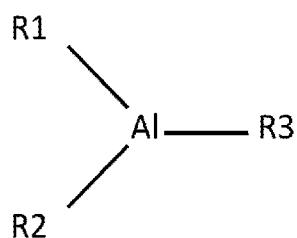
described in this disclosure should not be considered limited in their use to the dimerization of ethylene to 1-butene.

[0012] As described previously in this disclosure, embodiments of the described antifouling catalyst systems may comprise one or more titanate compounds. While several titanate compounds may be included in the antifouling catalyst system, in some embodiments a single titanate compound may be included in the antifouling catalyst system. In one or more embodiments, the titanate compound may be an alkyl titanate. An alkyl titanate may have the structure $Ti(OR)_4$ in which R is a branched or straight chain alkyl group. In one or more embodiments, each alkyl group may comprise from 2 to 8 carbons, where each R group may be the same or different. Suitable alkyl titanates may include tetraethyl titanate, tetraisopropyl titanate, tetra-n-butyl titanate (sometimes referred to as titanium butoxide or tetrabutyl orthotitanate), 2-tetraethylhexyl titanate. In one or more embodiments, the titanate compound of the antifouling catalyst system consists of tetra-n-butyl titanate.

[0013] As also described previously in this disclosure, embodiments of the described antifouling catalyst systems may comprise one or more aluminum compounds. While several aluminum compounds may be included in the antifouling catalyst system, in some embodiments a single aluminum compound may be included. In one or more embodiments, one or more aluminum alkyl compounds may be included in the antifouling catalyst system. Aluminum alkyl compounds may have a structure of AlR'_3 or AlR'_2H , where R' is a straight chain or branched alkane comprising from 1 to 20 carbons, or an aluminoxane structure (that is, a partial hydrolysate of trialkylaluminum compounds). For example, and not by way of limitation, suitable aluminum alkyl compounds may include triethylaluminum, tripropylaluminum, tri-isobutylaluminum, and trihexylaluminum. In one or more embodiments, the aluminum compound of the antifouling catalyst system consists of triethylaluminum.

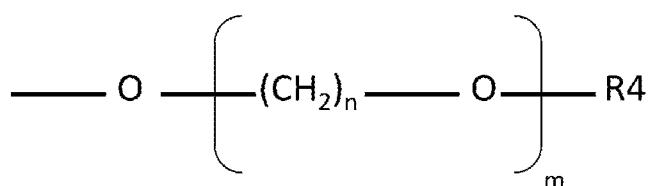
[0014] The antifouling catalyst systems may comprise one or more antifouling agents or derivatives thereof. As used herein, a derivative refers to a derivative structure of an antifouling agent, such as a dimer, trimer, oligomer, polymer, isomer, hydrolysate of an antifouling agent described in this disclosure. In one or more embodiments, an antifouling agent may comprise a central aluminum molecule bonded to all three of a first chemical group R1, a second chemical

group R2, and a third chemical group R3. Chemical Structure #1 depicts a generalized chemical structure of an antifouling agent.



- **Chemical Structure #1 – Generalized Antifouling Agent**

In one or more embodiments, one or more of R1, R2, and R3 are antifouling groups comprising the structure $-\text{O}((\text{CH}_2)_n\text{O})_m\text{R}_4$, where n is an integer from 1 to 20 (for example, 1 to 15, 1 to 10, 1 to 5, 1 to 4, 1 to 3, 1 to 2, 2 to 20, 3 to 20, 4 to 20, 5 to 20, 10 to 20, or 15 to 20), m is an integer from 1 to 100 (for example, 1 to 10, 1 to 20, 1 to 30, 1 to 40, 1 to 50, 1 to 75, 5 to 100, 10 to 100, 25 to 100, 50 to 100, or 75 to 100), and R4 is a hydrocarbyl group. The structure of the antifouling group, $-\text{O}((\text{CH}_2)_n\text{O})_m\text{R}_4$, is depicted in Chemical Structure #2. The central aluminum atom is bonded to a terminal oxygen of the antifouling group opposite of the R4 hydrocarbyl group. As used throughout this disclosure, a hydrocarbyl group refers to a chemical group that consists of hydrogen and carbon atoms. For example, a hydrocarbyl group may be branched or unbranched, and may comprise one or more alkane moieties, one or more alkene moieties, one or more alkyne moieties, or combinations thereof. Hydrocarbyl groups may include cyclic or aromatic moieties. In one or more embodiments, R4 may be a hydrocarbyl group having from 1 to 100 carbon atoms, such as from 5 to 50 carbon atoms, or from 12 to 28 carbon atoms.

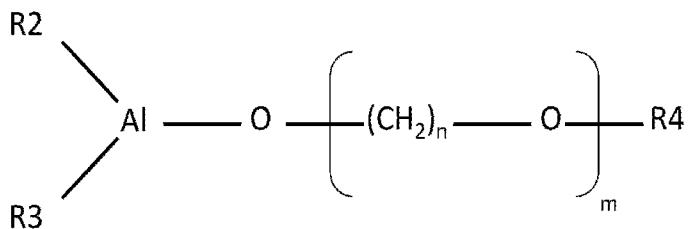


- **Chemical Structure #2 – Antifouling Group**

[0015] As previously described in this disclosure, one, two, or all three of R1, R2, and R3 may comprise the antifouling groups comprising the structure of Chemical Structure #2. In

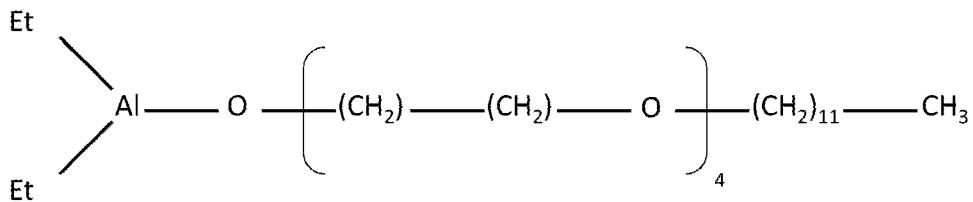
embodiments described in this disclosure, the chemical groups R1, R2, or R3 that do not comprise the antifouling group, if any, are hydrocarbyl groups. For example, R1 may be an antifouling group with the structure depicted in Chemical Structure #2 and R2 and R3 may be hydrocarbyl groups. In another embodiment, R1 and R2 may be antifouling groups with the structure depicted in Chemical Structure #2, and R3 may be a hydrocarbyl group. In another embodiment, R1, R2, and R3 may be antifouling groups with the structure depicted in Chemical Structure #2. When at least two of R1, R2, and R3 are hydrocarbyl groups, they may be identical to one another or may be different hydrocarbyl groups. Also, when two or more of R1, R2, or R3 are antifouling groups, the antifouling groups may be identical or chemically different. However, they will each have the generic structure depicted in Chemical Structure #2. R1, R2 and R3 that are hydrocarbyl groups may each have from 1 to 100 carbon atoms, such as, for example, from 1 to 50 carbon atoms. For example, if R1, R2, or R3 are hydrocarbyl groups, they may be straight chained alkanes such as methyl, ethyl, propyl, or butyl groups.

[0016] By way of example, if R1 is an antifouling group, and R2 and R3 are hydrocarbyl groups, the generalized structure of the antifouling agent can be represented by Chemical Structure #3.



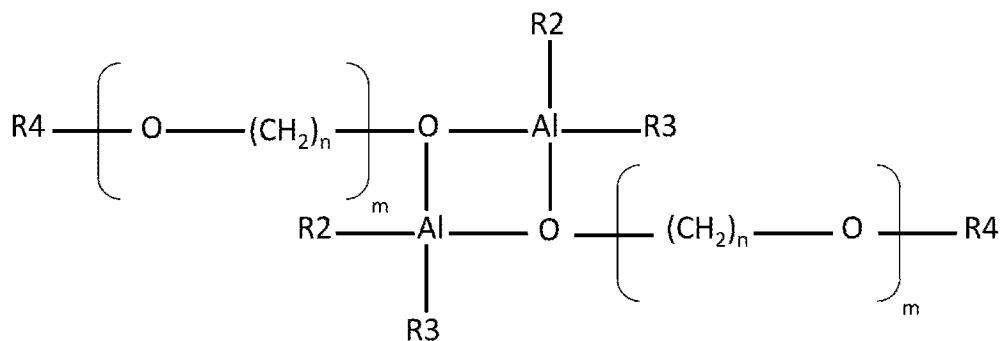
- **Chemical Structure #3 – Example of Generalized Antifouling Agent**

[0017] In one or more embodiments, the antifouling agent may comprise an R1 group that is an ethyl group, an R2 group that is an ethyl group, and an R3 that is an antifouling group having the structure $-\text{O}((\text{CH}_2)_n\text{O})_m\text{R4}$, where $n = 2$, $m = 4$, and R4 is a dodeyl group. Such an antifouling agent can be written as $(\text{CH}_3\text{CH}_2)_2\text{AlO}(\text{CH}_2\text{CH}_2\text{O})_4(\text{CH}_2)_{11}\text{CH}_3$, and has the chemical structure depicted in Chemical Structure #4, where “Et” represents an ethyl group.



- **Chemical Structure #4 – Example of Antifouling Agent**

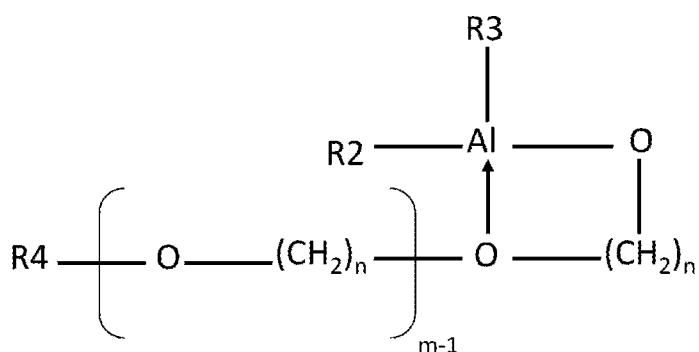
[0018] In one or more embodiments, the antifouling agent may be present as a dimerized form, referred to herein as an example of a derivative of an antifouling agent. A prepared antifouling agent may be present in both dimerized and non-dimerized (that is, non-bonded) form. For example, in a dimerized state, the antifouling agent may comprise a structure as shown in Chemical Structure #5. Chemical Structure #5 shows the dimerized embodiment of the antifouling agent structure depicted in Chemical Structure #3. In a dimerized embodiment, a bond may form between a central aluminum atom of an antifouling agent molecule and an oxygen atom of a neighboring antifouling agent molecule. It should be understood that while in Chemical Structures #5 the central aluminum atoms are bonded to the oxygen atom in the neighboring antifouling agent that is most near to its central aluminum atom, in other embodiments, this may not be the case, and the a central aluminum atom may bond with an oxygen atom of a neighboring antifouling agent which is not most near to its central aluminum atom.



- **Chemical Structure #5 – Example of Dimerized Antifouling Agent**

[0019] In one or more embodiments, the antifouling agent may be present in different isomer states, one such example depicted in Chemical Structure #6. An isomer is an example of a

derivative structure of an antifouling agent. For example, and as depicted in Chemical Structure #6, the central aluminum atom of an antifouling agent may be bonded to two oxygen atoms of a single antifouling group. It should be understood that while Chemical Structure #6 depicts an isomer where the two oxygen atoms most near to the central aluminum atom are bonded with the central aluminum atom, in other embodiments other isomers may form, such as an isomer formed when the central aluminum atom forms a bond with an oxygen atom which is not as close as another oxygen atom to the central aluminum atom in the antifouling agent molecule. For example, while Chemical Structure #6 shows a ring structure with 2 oxygen atoms and n carbon atoms, larger ring structures may form in other isomers, such as rings having three or more oxygen atoms. It should be understood that isomers of the antifouling agents described, such as that shown in Chemical Structure #6, are considered antifouling agents and fit into the base structure depicted in Chemical Structure #1. For instance, the existence of two oxygen atoms bonded to the central aluminum, where both oxygen atoms are part of an antifouling group, is considered to conform to the base structure depicted in Chemical Structure #1.



- **Chemical Structure #6 – Example of Isomer of Antifouling Agent**

[0020] In one or more embodiments, the antifouling catalyst systems may comprise more than one molecular species of antifouling agent. For example, the antifouling catalyst system may comprise antifouling agents with a varying number of antifouling groups. For example, some antifouling agent molecules may comprise none, one, two or three antifouling groups, while others comprise a different number of antifouling groups. The mixture of these antifouling agent species may form a bulk antifouling agent which can be characterized by its bulk molar ratio of hydrocarbyl groups to antifouling groups which are attached to the central aluminum atoms, respectively. For example, if half of the antifouling agent has one antifouling group and

two hydrocarbyl groups, and, the other half of the antifouling agent has two antifouling groups and one hydrocarbyl group, then the bulk molar ratio of hydrocarbyl groups to antifouling groups would be 1:1 because there is a bulk equal amount of hydrocarbyl groups to antifouling groups. In one or more embodiments, the bulk molar ratio of hydrocarbyl groups to antifouling groups may be from 1:1 to 20:1. Non-limiting examples of bulk molar ratios of hydrocarbyl groups to antifouling groups include from 1:1 to 2:1, from 1:1 to 3:1, from 1:1 to 4:1, from 1:1 to 5:1, from 1:1 to 10:1, from 1:1 to 15:1, from 2:1 to 20:1, from 3:1 to 20:1, from 4:1 to 20:1, from 5:1 to 20:1, from 10:1 to 20:1, or from 15:1 to 20:1. According to one or more embodiments, the bulk molar ratio of hydrocarbyl groups to antifouling groups is from 1.5 to 2.5, from 1.8 to 2.2, or 2.

[0021] In one or more embodiments, the antifouling catalyst system may comprise one or more ether compounds. The one or more ether compounds may include cyclic ethers such as, but not limited to, tetrahydrofuran (THF), a dioxane, a Tetrahydropyran (THP), or combinations thereof.

[0022] The antifouling catalyst systems may comprise at least one or more titanate compounds, one or more aluminum compounds, and one or more antifouling agents. In one or more embodiments, the molar ratio of total titanate compound to total aluminum compound may be from 1:10 to 1:1.5 (such as, for example, from 1:10 to 1:2, from 1:10 to 1:3, from 1:10 to 1:4, from 1:10 to 1:5, from 1:10 to 1:6, from 1:10 to 1:7, from 1:10 to 1:8, from 1:10 to 1:9, from 1:9 to 1:1.5, from 1:8 to 1:1.5, from 1:7 to 1:1.5, from 1:6 to 1:1.5, from 1:5 to 1:1.5, from 1:4 to 1:1.5, from 1:3 to 1:1.5, or from 1:2 to 1.5).

[0023] In one or more embodiments, the molar ratio of total titanate compounds to total antifouling agent may be from 1:5 to 1:0.01 (such as, for example, from 1:5 to 1:0.05, from 1:5 to 1:0.1, from 1:5 to 1:0.3, from 1:5 to 1:0.5, from 1:5 to 1:0.7, from 1:5 to 1:1, from 1:5 to 1:2, from 1:5 to 1:3, from 1:5 to 1:4, from 1:4 to 1:0.01, from 1:3 to 1:0.01, from 1:2 to 1:0.01, from 1:1 to 1:0.01, from 1:0.7 to 1:0.01, or from 1:0.3 to 1:0.01).

[0024] In one or more embodiments, the molar ratio of total titanate compounds to total ether compounds may be from 1:20 to 1:0 (such as, for example, from 1:15 to 1:0, from 1:10 to 1:0,

from 1:5 to 1:0, from 1:1 to 1:0, from 1:0.5 to 1:0, from 1:0.3 to 1:0, from 1:0.1 to 1:0, from 1:20 to 1:0.1, from 1:20 to 1:0.5, from 1:20 to 1:1, from 1:20 to 1:5, from 1:20 to 1:10).

[0025] It should be understood that the molar ratios of components of the antifouling catalyst systems described previously are representative of the total amount of each component of the antifouling catalyst system relative to the total amount of titanate compound, where the “total” amount refers to the molar amount of all species of the antifouling catalyst system which may be considered as a particular component type (that is, titanate compound, aluminum compound, ether compound, or antifouling agent). The total amount of a component may include two or more chemical species which are titanate compounds, aluminum compounds, ether compounds, or antifouling agents, respectively. It should also be understood that, as used in this disclosure, the total amount of aluminum compound does not include molecules that are considered as antifouling agents. Therefore, any species that is considered an antifouling agent as described in this disclosure does not contribute towards the total amount of aluminum compound even though the antifouling agent includes an aluminum central atom and may otherwise be considered as an aluminum-containing compound.

[0026] In one or more embodiments, the antifouling agent does not dealkylate, or is resistant to dealkylation as compared with other catalyst systems. Ethane releasing reactions may be undesirable, as they can contaminate a feed stream. In one or more embodiments, the antifouling agent does not deactivate the catalytic centers of one or more of the titanate compound or the aluminum compound.

[0027] According to another embodiment of the present disclosure, 1-butene may be produced. According to the method for 1-butene production, ethylene may be contacted with the antifouling catalyst system described previously to oligomerize the ethylene to form 1-butene. In one or more embodiments, the ethylene and antifouling catalyst system are supplied to a reactor and mixed. The reaction may be performed as a batch reaction or as a continuous process reaction, such as a continuous stir tank reactor process. According to embodiments, the pressure of the reactor may be from 5 bar to 100 bar, the reactor temperature may be from 30 degrees Celsius (°C) to 180 °C. However process conditions outside of these ranges are contemplated, especially in view of the specific design of the reactor system and concentrations of the reactants and catalysts.

Examples

[0028] The various embodiments of antifouling catalyst systems will be further clarified by the following examples. The examples are illustrative in nature, and should not be understood to limit the subject matter of the present disclosure.

[0029] To form an antifouling agent having the chemical structure $(CH_3CH_2)_2AlO(CH_2CH_2O)_4C_{12}H_{25}$ (shown as Chemical Structure #4), 10 milliliters (mL) of triethyl aluminum (1 molar (M) in hexane) was reacted with 10 mL of polyethylene glycol dodecyl ether (1 M in hexane). Specifically, polyethylene glycol dodecyl ether was first dried with anhydrous grade sodium sulfate to remove any residual moisture. The dried polyethylene dodecyl ether was then added drop-wise to the triethyl aluminum in a 30 mL flask. The reaction mixture was subsequently stirred for 15 minutes. The reaction was carried out in an inert atmosphere inside a glove box. Light color change and release of ethane gas were observed during the reaction. Other antifouling agents were produced though similar techniques which incorporated reactants suitable to achieve antifouling agents having varying values of n, m, and R4 as described in this disclosure with reference to antifouling groups.

[0030] To evaluate the anti-fouling effects of the antifouling catalyst systems described, ethylene oligomerization reactions were carried out and evaluated. Multiple sample antifouling catalyst systems were formulated. Detailed structure of the antifouling agents used, as well as ratios of are listed in Table 1. For the experiments, catalyst mixtures were used that contained titanium tetrabutoxide (denoted as “Ti” in Table 1), THF, triethyl aluminum (denoted as “TEAL” in Table 1), and antifouling agents (denoted as “AFA” in Table 1). The antifouling agents utilized are described previously in this disclosure and are depicted in Chemical Structure #3 (where for the experiments, R2 and R3 are ethyl groups, and n, m, and R4 are specified in Table 1). In addition to the catalyst mixtures containing antifouling agent, comparative examples which did not contain antifouling agent were tested and compared with the catalyst systems which included antifouling agents.

[0031] The components of the sample catalyst systems were prepared and transferred into metal charging cylinders in a glove box. The THF was premixed with the titanium tetrabutoxide (in samples where THF was included) and transferred to a charging cylinder, and the antifouling agent was premixed with the triethyl aluminum in heptane (1 M) utilized as a solvent. The

oligomerization reactions were conducted in an autoclave batch reactor unit (1000 mL volume). In a typical reaction run, the reactor vessel was vacuum purged with ultrapure nitrogen to remove oxygen and moisture. Then, the batch reactor was filled with anhydrous hexane and kept at 50 °C. The anti-fouling agent and triethyl aluminum solution in heptane (1M) was then introduced into the reaction vessel. Then, the pre-mixed solution containing titanium tetrabutoxide and THF was introduced into the reactor. The catalyst solution had a concentration of titanium tetrabutoxide of 1 micromolar. Following introduction of the components of the catalyst system, the reactor was pressurized to 2.3 mega-Pascals (MPa) with ethylene and the temperature of the reactor was set to 53 °C with a stirring rate of 300 rpm. The dimerization reaction was terminated by injecting 2 mL of ethanol after 30 minutes. The reactor was subsequently depressurized. The remaining solid polymer was filtered, dried overnight in an oven at 110 °C and weighed.

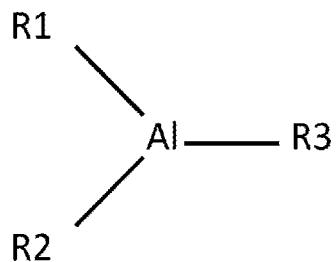
[0032] Table 1 shows the dimerization activity and weight of polymer deposit for reactions which utilized each of the sample catalyst systems. As is evident by the reaction data of Table 1, the addition of the antifouling additive greatly reduced polymer formation.

Table 1

	Molar Ratio of Ti:THF:TEAL:AFA	n	m	R4	Activity (grams of ethylene per hour per millimoles of titanium)	Polymer Produced (mg)
Comparative Example 1	1:4:7.5:0	N/A	N/A	N/A	221	200
Example 1	1:4:7:0.4	2	4	C ₁₂ H ₂₅ -n	291	35
Example 2	1:4:7.5:3	2	10	C ₁₈ H ₃₇ -n	224	21
Example 3	1:4:7.5:3	2	20	C ₁₈ H ₃₇ -n	228	78
Comparative Example 2	1:6:7.5:0	N/A	N/A	N/A	190	187
Example 4	1:6:7.5:0.6	2	4	C ₁₂ H ₂₅ -n	254	N/A
Comparative Example 3	1:6:7.5:0	N/A	N/A	N/A	278	91
Example 5	1:6:7.5:0.6	2	2	C ₁₈ H ₃₇ -n	276	4
Example 6	1:6:7.5:0.6	2	4	C ₁₂ H ₂₅ -n	289	6
Example 7	1:6:7.5:1	2	4	C ₁₂ H ₂₅ -n	263	4

CLAIMS

1. A catalyst system that reduces polymeric fouling, the catalyst system comprising:
at least one titanate compound;
at least one aluminum compound; and
at least one antifouling agent or a derivative thereof, where the antifouling agent comprises the structure:



where one or more of the chemical groups R1, R2, and R3 are antifouling groups comprising the structure $-\text{O}((\text{CH}_2)_n\text{O})_m\text{R4}$, where:

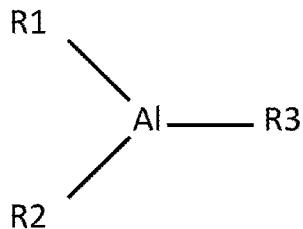
n is an integer from 1 to 20;
m is an integer from 1 to 100; and
R4 is a hydrocarbyl group; and

where the chemical groups R1, R2, or R3 that do not comprise the antifouling group, if any, are hydrocarbyl groups.

2. The catalyst system of claim 1, where n is from 1 to 5.
3. The catalyst system of claim 1, where m is from 1 to 20.
4. The catalyst system of claim 1, where R4 has from 1 to 100 carbon atoms.
5. The catalyst system of claim 1, further comprising an ether compound.
6. The catalyst system of claim 5, where the ether compound is tetrahydrofuran, a dioxane, or tetrahydropyran.

7. The catalyst system of claim 1, where at least one of the titanate compounds is an alkyl titanate.
8. The catalyst system of claim 7, where the alkyl titanate has the structure $Ti(OR)_4$, where R is a branched or straight chain alkyl radical comprising from 2 to 8 carbon atoms.
9. The catalyst system of claim 7, where the alkyl titanate is chosen from tetraethyl titanate, tetraisopropyl titanate, tetra-n-butyl titanate, or 2-tetraethylhexyl titanate.
10. The catalyst system of claim 1, where at least one of the aluminum compounds has the structure AlR'_3 or AlR'_2H , where R' is a branched or straight chain alkyl radical comprising from 2 to 8 carbon atoms.
11. The catalyst system of claim 1, where at least one of the aluminum compounds is chosen from triethylaluminum, tripropylaluminum, tri-iso-butylaluminum, trihexylaluminum, or an aluminoxane.
12. The catalyst system of claim 1, where a molar ratio of total titanate compound to total aluminum compound is from 1:10 to 1:1.5.
13. The catalyst system of claim 1, where a molar ratio of total titanate compound to total antifouling agent is from 1:5 to 1:0.01.
14. The catalyst system of claim 1, where a molar ratio of total titanate compound to total ether compound is from 1:10 to 1:0.
15. A method of producing 1-butene comprising:
contacting ethylene with a catalyst system to oligomerize the ethylene to form 1-butene, where the catalyst system comprises:
at least one titanate compound;
at least one aluminum compound; and

at least one antifouling agent or derivative thereof, where the antifouling agent comprises the structure:



where one or more of the chemical groups R1, R2, and R3 are antifouling groups comprising the structure $-\text{O}((\text{CH}_2)_n\text{O})_m\text{R}_4$, where:

n is an integer from 1 to 20;

m is an integer from 1 to 100; and

R4 is a hydrocarbyl group;

where the chemical groups R1, R2, or R3 that do not comprise the antifouling group, if any, are hydrocarbyl groups.

16. The method of claim 15, where a molar ratio of total titanate compound to total ether compound is from 1:10 to 1:0.

17. The method of claim 15, where n is from 1 to 5.

18. The method of claim 15, where m is from 1 to 20.

19. The method of claim 15, where R4 has from 1 to 100 carbon atoms.

20. The method of claim 15, further comprising an ether compound.

21. The method of claim 20, where the ether compound is tetrahydrofuran, a dioxane, or tetrahydropyran.

22. The method of claim 15, where at least one of the titanate compounds is an alkyl titanate.

23. The method of claim 22, where the alkyl titanate has the structure $Ti(OR)_4$, where R is a branched or straight chain alkyl radical comprising from 2 to 8 carbon atoms.

24. The method of claim 22, where the alkyl titanate is chosen from tetraethyl titanate, tetraisopropyl titanate, tetra-n-butyl titanate, or 2-tetraethylhexyl titanate.

25. The method of claim 15, where at least one of the aluminum compounds has the structure AlR'_3 or AlR'_2H , where R' is a branched or straight chain alkyl radical comprising from 2 to 8 carbon atoms.

26. The method of claim 15, where at least one of the aluminum compounds is chosen from triethylaluminum, tripropylaluminum, tri-iso-butylaluminum, trihexylaluminum, or an aluminoxane.

27. The method of claim 15, where a molar ratio of total titanate compound to total aluminum compound is from 1:10 to 1:1.5.

28. The method of claim 15, where a molar ratio of total titanate compound to total antifouling agent is from 1:5 to 1:0.01.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/012299

A. CLASSIFICATION OF SUBJECT MATTER	INV. B01J31/12	B01J31/14	B01J31/02	C07C2/30	C07C11/08
ADD.					

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J C07C

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 792 895 A (INST FRANCAIS DU PETROLE [FR]; SAUDI BASIC IND CORP SABIC [SA]) 11 August 1998 (1998-08-11) claims 1-10,14,16-18; examples 2-6,8; tables 1,2 ----- US 2014/088331 A1 (AXENS [FR]) 27 March 2014 (2014-03-27) paragraphs [0025] - [0032], [0036], [0037]; claims 2-4,6; example 1 ----- -/-	1-28
X		1-28

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "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)
- "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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

16 May 2017

08/06/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Goebel, Matthias

INTERNATIONAL SEARCH REPORT

International application No PCT/US2017/012299

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>STEPHEN J. OBREY ET AL: "A Lewis Base Promoted Alkyl/Alkoxide Ligand Redistribution: Reaction of [Me 2 Al([mu]-OCPh 3)] 2 with THF", ORGANOMETALLICS, vol. 20, no. 24, 1 November 2001 (2001-11-01), pages 5119-5124, XP055373036, US ISSN: 0276-7333, DOI: 10.1021/om010394i abstract page 5119 - page 5122; figure 4</p> <p>-----</p>	1-28
A	<p>T Mole: "ORGANOALUMINIUM COMPOUNDS - XI. REACTION OF TRIALKYLALUMINIUMS WITH DIALKYALUMINIUM ALKOXIDES", Australian Journal of Chemistry, 1 January 1966 (1966-01-01), pages 381-386, XP055373038, DOI: https://doi.org/10.1071/CH9660381 Retrieved from the Internet: URL:http://www.publish.csiro.au/ch/pdf/CH9660381 [retrieved on 2017-05-15] the whole document</p> <p>-----</p>	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/012299

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
US 5792895	A 11-08-1998	DE	69703909 D1		22-02-2001
		DE	69703909 T2		26-04-2001
		EP	0803491 A1		29-10-1997
		FR	2748020 A1		31-10-1997
		JP	4113993 B2		09-07-2008
		JP	H1045637 A		17-02-1998
		US	5792895 A		11-08-1998
<hr/>					
US 2014088331	A1 27-03-2014	CN	103724149 A		16-04-2014
		EP	2711349 A1		26-03-2014
		FR	2995893 A1		28-03-2014
		JP	2014062094 A		10-04-2014
		KR	20140038903 A		31-03-2014
		US	2014088331 A1		27-03-2014
<hr/>					