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(71) Applicants *(for all designated States except US)*: **LINDE AG** [DE/DE]; Klosterhofstrasse 1, 80331 München (DE). **SAUDI BASIC INDUSTRIES CORPORATION** [SA/SA]; P.O. Box 5101, 11422 Riyadh (SA).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **FRITZ, Peter, M.** [DE/DE]; Truderinger Str. 21, 82009 Unterhaching (DE). **BÖLT, Heinz** [DE/DE]; Kanalstrasse 21, 82515 Wolfratshausen (DE). **MEISWINKEL, Andreas** [DE/DE]; Ludwigshöher Strasse 14, 81479 Munich (DE). **TAUBE, Carsten** [DE/DE]; Baldestrasse 31C, 85560 Ebersberg (DE). **WINKLER, Florian** [DE/DE]; Holzstrasse 49, 80469 Munich (DE). **GÖKE, Volker** [DE/DE]; Am Loisachbogen 7e, 82515 Wolfratshausen (DE). **MÜLLER, Wolfgang** [DE/DE]; Jasperallee 36, 81245 Munich (DE). **WÖHL, Anina** [DE/DE]; Wolfratshausener Strasse 86a, 82049 Pullach (DE). **SCHNEIDER, Richard** [DE/DE]; Kirchtalstrasse 2B, 82449 Uffing (DE). **ROSENTHAL, Uwe** [DE/DE]; Hahnenkamp 9, 18069 Lambrechtshagen (DE). **FRITZ, Helmut** [DE/DE]; Zillertalstrasse 31, 81373 Munich (DE). **MÜLLER, Bernd, H.** [DE/DE]; Gellertstrasse 7, 18057 Rostock (DE). **PEULECKE, Normen** [DE/DE]; Vitus-Bering-Str. 34, 18106 Rostock (DE). **PEITZ, Stephan** [DE/DE]; Klosterbachstrasse 13, 18057 Rostock (DE). **ALURI, Bhaskar, Reddy** [IN/DE]; Bergstr. 7a, Apartment 301, 18057 Rostock (DE). **AL-HAZMI, Mohammed** [SA/SA]; Saudi Basic Industries Corporation, P.O. Box 5101, 11422 Riyadh (SA). **AZAM, Shahid, Majeed** [IN/SA]; Saudi Basic Industries Corporation, Riyadh Industrial Area 2, Al-Kharj Road, P.O. Box 42503 (SA). **MOSA, Fuad** [SA/SA]; Saudi Basic Industries Corporation, Riyadh Industrial Area 2, Al-Kharj Road, P.O. Box 42503 (SA). **AL-DUGATHIER, Abdellah** [SA/SA]; Saudi Basic Industries Corporation, Riyadh Industrial Area 2, Al-Kharj Road, P.O. Box 42503 (SA).

(74) Agents: **SCHOLZ, Volker** et al.; Boehmert & Boehmert, Hollerallee 32, 28209 Bremen (DE).

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(54) **Title**: METHOD FOR PREPARING LINEAR ALPHA-OLEFINS

(57) **Abstract**: The present invention relates to a method for preparing linear alpha-olefins (LAO) by oligomerization of ethylene in the presence of a solvent and homogeneous catalyst, comprising the steps of: (i) feeding ethylene, solvent and catalyst into an oligomerization reactor, (ii) oligomerizing the ethylene in the reactor, (iii) removing a reactor outlet stream comprising solvent, linear alpha-olefins, optionally unreacted ethylene and catalyst from the reactor via a reactor outlet piping system, (iv) dosing at least one additive selected from the group consisting of alcohols, polyethylene glycols, polyethylene glycol monoethers, polyethylene glycol diethers, polyamines, amines, amino alcohols and surfactants, (v) transferring the reactor outlet stream containing the additive to a catalyst deactivation and removal section, and (vi) deactivating the catalyst with caustic and removing the deactivated catalyst from the reactor outlet stream, wherein the residence time of the additive in the reactor outlet stream prior to mixing with caustic is at least 1 second preferably at least 5 seconds, more preferably at least 10 seconds.

Method for preparing linear alpha-olefins

Description

The present invention relates to a method for preparing linear alpha-olefins (LAO).

Processes for the oligomerization of ethylene utilizing homogeneous catalysts are widely known. For example, DE 43 38 414 C1 discloses a process for the oligomerization of ethylene to obtain linear alpha-olefins, where ethylene is catalytically converted in an empty tubular reactor utilizing a catalyst comprising a zirconium component and an aluminum component. The process is advantageously carried out in a continuous mode wherein gaseous and liquid outlet streams are obtained. The liquid outlet stream usually contains solvent, catalyst, dissolved ethylene and linear alpha-olefins. The catalyst may be preferably deactivated by caustic. Preferably, the deactivated catalyst is also extracted from the phase containing solvent, ethylene and alpha-olefins.

DE 198 07 226 A1 discloses the deactivation of the oligomerization catalyst with an aqueous solution of sodium hydroxide (caustic), wherein the deactivated catalyst is transferred from the organic phase into the aqueous phase.

From operational experience it was learned that the deactivation step has to be performed fast and effectively. Otherwise, there is a chance of product degradation by unwanted side reactions having influence on the product purity. Catalyst removal efficiency can be enhanced by static or active mixing devices. However, these systems turned out to be not optimal for the application due to high installations costs, respective intensive maintenance requirements.

As further disadvantage of the known processes was found that both formation of organic chlorides as well as of alkylated toluenes by Friedel-Crafts-alkylation occurs.

It is therefore an object of the present invention to provide a method for preparing linear alpha-olefins which overcomes the drawbacks of the prior art, especially to provide a method including deactivation and removal of the catalyst resulting in an improved product purity, suppression of unwanted side reactions, less energy requirements for mixing, no requirement for sophisticated mixing devices and allowing online cleaning of piping and equipment. Also, the formation of organic chlorides and of alkylated toluenes by Friedel-Crafts-alkylation shall be prevented.

This object is achieved by a method for preparing linear alpha-olefins (LAO) by oligomerization of ethylene in the presence of a solvent and homogeneous catalyst, comprising the steps of:

(i) feeding ethylene, solvent and catalyst into an oligomerization reactor,

(ii) oligomerizing the ethylene in the reactor,

(iii) removing a reactor outlet stream comprising solvent, linear alpha-olefins, optionally unreacted ethylene and catalyst from the reactor via a reactor outlet piping system,

(iv) dosing at least one additive selected from the group consisting of alcohols, polyethylene glycols, polyethylene glycol monoethers, polyethylene glycol diethers, polyamines, amines, amino alcohols and surfactants,

(v) transferring the reactor outlet stream containing the additive to a catalyst deactivation and removal section, and

(vi) deactivating the catalyst with caustic and removing the deactivated catalyst from the reactor outlet stream,

wherein the residence time of the additive in the reactor outlet stream prior to mixing with caustic is at least 1 second, preferably at least 5 seconds, more preferably at least 10 seconds.

It is preferred that the additive is selected from MOR, HO-$(CH_2$-$CH_2)_n$-OH, HO-$(CH_2$-$CH_2)_n$-OR, RO-$(CH_2$-$CH_2)_n$-OR, R'_2N-$[(CH_2)_n]$-NR'_2, R'_3N, R'_2N-$[(CH_2)_n]$-OR′ with M = alkali metal, R = alkyl or aryl, R′ = H, alkyl or aryl and n = 3-300.

Preferably, the amine is an organic amine, preferably a primary, secondary, tertiary or cyclic amine, more preferably selected from t-butyl amine, triethyl amine, cyclopentyl amine, t-octyl amine, n-heptyl amine, 2-heptyl amine, hexyl amine, 2-ethylhexyl amine, dihexyl amine, 1,6-diamino hexane, tributyl amine, 1,8-diamino octane, n-dodecyl amine, 3-ethylheptyl amine and tris-2-ethyl hexyl amine.

More preferred the additive is added continously into the reactor outlet stream.

In one embodiment, the additive is added in an amount of 500 to 5000 wt ppm referred to the flow rate of the reactor outlet stream.

The amount of dosing is determined by the following two issues:

- The amount required in a certain stochiometric ratio to the catalyst and cocatalyst rates as introduced into the LAO reactor

- The amount obtained from practical operational experience in order to realize the described online cleaning effects for the reactor outlet piping.

Even preferred, the additive is soluble in an organic phase containing linear alpha-olefins.

In a further preferred embodiment the additive is substantially insoluble or has a low solubility in water or a mixture of water and caustic.

The additive may be preferably removed from the reactor outlet stream or a product fraction by distillation, extraction, adsorption or ion exchange.

More preferably, the removed additive is recycled into the reactor outlet stream when removed from the reactor.

In one preferred embodiment the additive is mixed with the reactor outlet stream by means of a mixing device, preferably a static mixer, a dynamic mixer, an ultrasonic mixer or a Venturi mixing nozzle.

It is preferred that the catalyst comprises a zirconium salt of organic acid and at least one organoaluminum compound.

Even preferred, the zirconium salt has the formula $ZrCl_{4-m}X_m$, wherein X = OCOR or OSO_3R' with R and R' being independently alkyl, alkene or aryl, preferably phenyl, and wherein $0 \leq m \leq 4$.

It is further preferable that the at least one aluminum compound has the general formula $R^1{}_nAl_{3-n}$ or $Al_2Y_3R^1{}_3$, wherein R^1 represents an alkyl group having from 1 to 20 carbon atoms, Y represents Cl, Br or I, n is any number within the range $1 \leq n \leq 2$.

Surprisingly, it was found that dosing of an additive selected from the group as disclosed above into the reactor outlet stream prior to the mixing of the reactor outlet stream with aqueous caustic only under certain, very specific conditions significantly improves the efficiency of the catalyst removal section without obtaining any unwanted side reactions. Thus, the product purity can be improved. It was surprisingly found that there is a minimum residence time required for the additive until its impact on the system is evoluted. This minimum residence time is at least 1 second.

It was also found that a simple combination of amine dosing and a caustic deactivation will not at all be sufficient for the envisaged purpose. It is a main feature of the invention that surprisingly a certain minimum residence time between the dosing of the additive and the caustic is required.

All the additives disclosed are found to be responsible to prevent Friedel-Crafts-alkylations of the solvent utilized, as well as the formation of organic chlorides, especially by preventing the formation of HCl which forms with LAOs the organic chlorides, or with the formed organic chlorides and the solvent, preferably toluene, alkylated solvents.

Further, it is important to note that the location of addition of the additive is essential. For example, additive dosing into the caustic stream will not work, as well as simultaneous mixing of all streams, i.e. additive stream, reactor outlet stream and caustic stream, will not resolve all these issues. Rather, it is absolutely necessary that the additive is introduced into the reactor outlet stream close to the LAO reactor outlet, with a sufficient residence time prior to the mixing point with the caustic stream.

Without wishing to be bound to any theory, it is believed that the additive utilized in the inventive method may reduce the interfacial tension between the hydrocarbon LAO phase and the aqueous caustic phase, leading to the formation of smaller droplet sizes, and finally enhancing the solubility of the catalyst deactivation products in the aqueous caustic phase.

Only in case that the additive is dosed into the reactor outlet stream as illustrated, the following benefits can be achieved:

- effective mixing of LAO/caustic turned out to be much easier,

- product purities were improved due to suppression of unwanted side reactions,

- inhomogenity and hot spots in the LAO/caustic mixing step were not observed anymore, and

- maintenance requirements for a mixer are reduced.

- fouling/plugging of LAO reactor outlet piping is avoided due to the online-cleaning effect (i.e. removal of rust particles and materials from equipment surfaces, and pipe walls, by utilization of tenside effects).

Additional features and advantages of the present invention will now become apparent from the detailed description of a preferred embodiment thereof.

Ethylene is oligomerized in a suitable reactor, for example an empty tubular reactor as disclosed in DE 43 38 414 C1, utilizing a catalyst comprising a zirconium compound and an aluminum component. A suitable zirconium component is zirconium tetraisobutyrate, and a suitable aluminum component is ethyl aluminum sesquichloride.

The oligomerization is carried out under conditions (temperature, pressure, etc.) known in the art. Ethylene, solvent and catalyst are introduced and oligomerization is initiated. From the reactor, a liquid organic outlet stream is discharged into a reactor outlet piping system containing solvent, for example toluene, catalyst, ethylene dissolved in the solvent, and linear alpha-olefins. To this liquid organic outlet stream is dosed an additive selected from the group of non-ionic surfactants and amines, for example n-dodecyl amine. Mixing of the reactor outlet stream and the additive is for at least 1 second, prior to the addition of caustic thereto in a catalyst deactivation and removal section. However, the residence time shall not exceed a period of 100 seconds, since otherwise the additive is already deactivated by undergoing of different unwanted reaction steps and has lost its activity for the envisaged positive effects. The catalyst is then deactivated by caustic and removed from the outlet stream. The caustic phase may contain alkali metal hydroxide, preferably NaOH and/or KOH. After deactivation the deactivated catalyst will be present in the aqueous phase and can be removed as known the art.

After the catalyst deactivation and removal section, the amine can be removed from the LAO products (the remaining reactor outlet stream) by conventional distillation, extraction, ion

exchange or adsorption. Remaining traces of the amine in the products can be additionally removed by adequate guard adsorbers, depending on the required product specification.

The prevention of Friedel-Crafts-alkylation was demonstrated by the following experiments:

Laboratory Experiment No 1: Basic experiment without additive

In the laboratory 20 ml toluene, 10 ml 1-hexene, 5 ml EASC solution and 20 ml ZrCl4 solution were mixed in a flask at ambient temperature and under inert nitrogen atmosphere.

Under intensive stirring the mixture was quenched with 50 ml sodium hydroxide solution of 20 wt%.

Then the stirring has been switched off. After the phase separation of the hydrocarbon phase and the aqueous phase by gravity the hydrocarbon phase has been analyzed and shows high quantities of alkylated toluene.

Laboratory Experiment No 2: Experiment with an amine as an additive (30 seconds residence time)

In the laboratory 20 ml toluene, 10 ml 1-hexene, 5 ml EASC solution and 20 ml ZrCl4 solution and 1 ml of ethyl-hexyl-amine were mixed in a flask at ambient temperature and under inert nitrogen atmosphere for 30 seconds.

Under intensive stirring the mixture was quenched with 50 ml sodium hydroxide solution of 20 wt%.

Then the stirring has been switched off. After the phase separation of the hydrocarbon phase and the aqueous phase by gravity the hydrocarbon phase has been analyzed and shows no alkylated toluene.

Laboratory Experiment No 3: Experiment with amine as an additive (simultaneous addition)

In the laboratory 10 ml toluene, 10 ml 1-hexene, 5 ml EASC solution and 20 ml ZrCl4 solution were mixed in a flask at ambient temperature and under inert nitrogen atmosphere. In a second flask 10 ml toluene and 1 ml of ethyl-hexyl-amine were mixed.

Under intensive stirring both mixtures were poured in a 50 ml sodium hydroxide solution of 20 wt% simultaneously.

Then the stirring has been switched off. After the phase separation of the hydrocarbon phase and the aqueous phase by gravity the hydrocarbon phase has been analyzed and shows some alkylated toluene but less than in Experiment No 1.

Laboratory Experiment No 4: Experiment with amine as an additive in the sodium hydroxide solution

In the laboratory 20 ml toluene, 10 ml 1-hexene, 5 ml EASC solution and 20 ml ZrCl4 solution were mixed in a flask at ambient temperature and under inert nitrogen atmosphere.

Under intensive stirring this mixture was quenched with a mixture of 50 ml sodium hydroxide solution of 20 wt% and 1 ml of ethyl-hexyl-amine.

Then the stirring has been switched off. After the phase separation of the hydrocarbon phase and the aqueous phase by gravity the hydrocarbon phase has been analyzed and shows almost the same amount of alkylated toluene as in Experiment No 1.

These simple experiments clearly confirm the importance and positive effect of the combination of an additive and the caustic for the prevention of undesired side reactions in catalyst deactivation and removal section of the LAO process. It becomes clear that the positive effect of the additive is also a function of the residence time of the additive in the reactor outlet stream prior to mixing with caustic.

The necessity of an adequate residence time for the achievement of a positive impact on the formation of alkylated toluene can also be seen in the attached graph, which has prepared based on analyses from laboratory experiments.

The features disclosed in the following description and in the claims may, both separately and in any combination thereof, be material for realizing the invention in diverse forms thereof.

Claims

1. Method for preparing linear alpha-olefins (LAO) by oligomerization of ethylene in the presence of a solvent and homogeneous catalyst, comprising the steps of:

(i) feeding ethylene, solvent and catalyst into an oligomerization reactor,

(ii) oligomerizing the ethylene in the reactor,

(iii) removing a reactor outlet stream comprising solvent, linear alpha-olefins, optionally unreacted ethylene and catalyst from the reactor via a reactor outlet piping system,

(iv) dosing at least one additive selected from the group consisting of alcohols, polyethylene glycols, polyethylene glycol monoethers, polyethylene glycol di-ethers, polyamines, amines, amino alcohols and surfactants,

(v) transferring the reactor outlet stream containing the additive to a catalyst deactivation and removal section, and

(vi) deactivating the catalyst with caustic and removing the deactivated catalyst from the reactor outlet stream,

wherein the residence time of the additive in the reactor outlet stream prior to mixing with caustic is at least 1 second, preferably at least 5 seconds, more preferably at least 10 seconds.

2. Method according to claim 1, wherein the additive is selected from MOR, HO-$(CH_2$-$CH_2)_n$-OH, HO-$(CH_2$-$CH_2)_n$-OR, RO-$(CH_2$-$CH_2)_n$-OR, R'_2N-$[(CH_2)_n]$-NR'_2, R'_3N,

R'_2N-$[(CH_2)_n]$-OR′ with M = alkali metal, R = alkyl or aryl, R′ = H, alkyl or aryl and n = 3-300.

3. Method according to claim 1 or 2, wherein the amine is an organic amine, preferably a primary, secondary, tertiary or cyclic amine, more preferably selected from t-butyl amine, triethyl amine, cyclopentyl amine, t-octyl amine, n-heptyl amine, 2-heptyl amine, hexyl amine, 2-ethylhexyl amine, dihexyl amine, 1,6-diamino hexane, tributyl amine, 1,8-diamino octane, n-dodecyl amine, 3-ethylheptyl amine and tris-2-ethyl hexyl amine.

4. Method according to any of the preceding claims, wherein the additive is added continously into the reactor outlet stream.

5. Method according to any of the preceding claims, wherein the additive is added in an amount of 500 to 5000 wt ppm.

6. Method according to any of the preceding claims, wherein the additive is soluble in an organic phase containing linear alpha-olefins.

7. Method according to any of the preceding claims, wherein the additive is substantially insoluble or has a solubility in water or a mixture of water and caustic of less than 5 mol%.

8. Method according to any of the preceding claims, wherein the additive is removed from the reactor outlet stream or a product fraction by distillation, extraction, adsorption or ion exchange.

9. Method according to claim 8, wherein the removed additive is recycled into the reactor outlet stream removed from the reactor.

10. Method according to any of the preceding claims, wherein the additive is mixed with the reactor outlet stream by means of a mixing device, preferably a static mixer, a dynamic mixer, an ultrasonic mixer or a Venturi mixing nozzle.

11. Method according to any of the preceding claims, wherein the catalyst comprises a zirconium salt of organic acid and at least one organoaluminum compound.

12. Method according to claim 11, wherein the zirconium salt has the formula $ZrCl_{4-m}X_m$, wherein X = OCOR or OSO_3R' with R and R' being independently alkyl, alkene or aryl, preferably phenyl, and wherein $0 \leq m \leq 4$.

13. Method according to any of the claims 11 or 12 wherein the at least one aluminum compound has the general formula $R^1{}_nAl_{3-n}$ or $Al_2Y_3R^1{}_3$, wherein R^1 represents an alkyl group having from 1 to 20 carbon atoms, Y represents Cl, Br or I, n is any number within the range $1 \leq n \leq 2$.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C2/30 C07C11/02
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)
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 practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 811 619 A (COMMEREUC DOMINIQUE [FR] ET AL) 22 September 1998 (1998-09-22) examples 5,6	1-13
X	FR 2 857 964 A (INST FRANCAIS DU PETROLE [FR]) 28 January 2005 (2005-01-28) page 3, lines 3-22 example 2 claim 6	1-13
X	EP 0 241 596 A (IDEMITSU PETROCHEMICAL CO [JP]) 21 October 1987 (1987-10-21) page 12, line 5 - page 13, line 1	1-13

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

☒ See patent family annex.

* Special categories of cited documents :

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Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Götz, Gerhard

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5811619 A	22-09-1998	CA 2156843 A1	20-07-1995
		CN 1122130 A	08-05-1996
		DE 69502136 D1	28-05-1998
		DE 69502136 T2	13-08-1998
		EP 0689528 A1	03-01-1996
		FR 2715154 A1	21-07-1995
		WO 9519332 A1	20-07-1995
		JP 8507553 T	13-08-1996
FR 2857964 A	28-01-2005	NONE	
EP 0241596 A	21-10-1987	DE 3675385 D1	06-12-1990
		US 4783573 A	08-11-1988