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(54) **Title:** METHOD FOR DEACTIVATION OF AN ORGANOMETALLIC CATALYST AND REACTOR SYSTEM THEREFOR

(57) **Abstract:** The present invention relates to a method for deactivation of an organometallic catalyst utilized in a catalyzed process, characterized in that a catalyst-containing outlet stream of a process reactor is subjected to a temperature of at least 160°C in a heating device; and a reactor system therefor.

Method for deactivation of an organometallic catalyst and reactor system therefore

Description

The present invention relates to a method for deactivation of an organometallic catalyst utilized in a catalyzed process and a reactor system therefore.

Organometallic catalysts are widely utilized in homogenously and heterogenously catalyzed processes, such as the oligomerisation of ethylene, to obtain linear alpha-olefins.

For example, DE 43 38 414 C1 discloses a process for the production of linear alpha-olefins by oligomerizing of ethylene in the presence of an organic solvent and a homogenous catalyst. This process is carried out in an empty tubular reactor providing an outlet stream comprising solvent, catalyst, dissolved ethylene and linear alpha-olefins. As further activity of the catalyst in equipment parts following the process reactor shall be avoided, the catalyst has to be deactivated within a very short time period. This deactivation may be achieved according to the prior art by the addition of water, alcohol or fatty acid.

Additionally, DE 198 07 226 A1 discloses a process for deactivation of a catalyst wherein the active catalyst is mixed with a solution of a metal hydroxide in a protonic solvent, to quench the catalyst.

The methods for deactivation of an organometallic catalyst known in the prior art show the disadvantages that they require costly materials of construction, especially if caustic and water are applied, and also generate substantial amounts of inorganic wastes.

It is an object of the present invention to provide a method for deactivation of an organometallic catalyst utilized in a homogenously catalyzed process, which method overcomes the disadvan-

tages of the prior art, especially providing a method avoiding cost intensive extraction systems and deactivation compounds together with substantial amounts of waste.

It is a further object of the present invention to provide a reactor system for carrying out the inventive method.

This object is achieved in that the catalyst-containing outlet stream of a process reactor is subjected to a temperature of at least 160°C in a heating device.

Surprisingly, it was found that the organometallic catalyst utilized in a homogenously catalyzed process may be irreversibly deactivated by thermal treatment of the catalyst at a temperature of at least 160°C. Preferably, the catalyst is rapidly heated to that temperature.

Utilizing the method according to the present invention, cost-intensive extraction systems, such as caustic/water, are completely eliminated. Further, the waste generated is minimized and the catalyst components may be recovered.

Of course, the inventive method is applicable to all homogenously catalyzed reactions, such as oligomerization of ethylene, oxosynthesis and liquid phase polymerization, however its use in the oligomerization of ethylene is preferred.

Preferably, the catalyst comprises a zirconium salt of organic acids and at least one organoaluminum compound.

More preferably, 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 phenyl, and wherein $0 < m < 4$.

In one embodiment, the at least one aluminum compound is $Al(C_2H_5)_3$, $Al_2Cl_3(C_2H_5)_3$ or $AlCl(C_2H_5)_2$.

Most preferably, the heating device is a thin film evaporator or a heat exchanger and a flash drum.

Further, the outlet stream may comprise solvent, catalyst, dissolved ethylene and linear alpha-olefins.

In this regard, the solvent may be selected from toluene, benzene and heptane, wherein toluene being preferred.

Further, it is preferred that the deactivated catalyst is separated from the outlet stream.

More preferably, the residence time of the catalyst-containing outlet stream in the heating device is from about 1 millisecond to about 1 minute.

Additionally, the object is achieved by a reactor system for catalyzed processes comprising a reactor and a heating device connected thereto to heat a catalyst-containing outlet stream of the reactor to a temperature of at least 160°C.

Finally, it is preferred that the heating device is a thin film evaporator or a heat exchanger and a flash drum.

Additional features and advantages of the inventive method will become apparent from the following detailed description of an exemplary embodiment of the inventive method in the process of oligomerisation of ethylene.

In the process of oligomerisation of ethylene to obtain linear alpha-olefins ethylene is oligomerized in a reactor in the presence of a solvent and a homogenous organometallic catalyst. From the oligomerisation reactor is preferably taken via a first line a mixture of ethylene and light alpha-olefins, together with some toluene which has been used as solvent. Via a second line a liquid mixture of toluene, catalyst, dissolved ethylene and linear alpha-olefins is discharged. To avoid further activity of the catalyst in the equipment parts following the oligomerisation reactor, it is essential to deactivate the catalyst as soon as possible. According to the inventive method this is achieved by subjecting this catalyst-containing outlet stream from the oligomerisation reactor to a temperature of at least 160°C in a heating device. Preferably, such a heating device may be a thin film evaporator or a heat exchanger and a flash drum which are able to heat the outlet stream rapidly to the desired temperature. At this temperature, the active catalytic components contained in the outlet stream are irreversibly destructed.

Thus, the inventive reactor system comprises a reactor and a heating device connected thereto, so that the catalyst-containing outlet stream from the reactor may be transferred into the heating device to heat the outlet stream to a temperature of at least 160°C. Most preferably, the residence time of the outlet stream in the heating device is from about 1 millisecond to about 1 minute.

It was found that the linear alpha olefins also present in the outlet stream are stable in a temperature range of 60 to about 300°C, so that the treatment of the outlet stream at a temperature of at least 160°C is not detrimental for the linear-alpha olefins to be obtained.

After heat treatment in the heating device, the outlet stream now containing deactivated catalyst components may be further processed according to the prior art processes, i.e. the catalyst components may be separated from the outlet stream and the linear alpha-olefins may be fractionated.

The features disclosed in the foregoing description or 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 deactivation of an organometallic catalyst utilized in a catalyzed process, characterized in that a catalyst-containing outlet stream of a process reactor is subjected to a temperature of at least 160°C in a heating device.

2. Method according to claim 1, wherein the process carried out in the process reactor is the homogenously catalyzed oligomerization of ethylene, an oxosynthesis or a liquid phase polymerization.

3. Method according to claim 2, wherein the process is the oligomerization of ethylene.

4. Method according to claim 3, wherein the catalyst comprises a zirconium salt of organic acids and at least one organoaluminum compound.

5. Method according to claim 4, 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 phenyl, and wherein $0 < m < 4$.

6. Method according to claim 4, wherein the at least one aluminum compound is $Al(C_2H_5)_3$, $Al_2Cl(C_2H_5)_3$ or $AlCl(C_2H_5)_2$.

7. Method according to any of the preceding claims, wherein the heating device is a thin film evaporator or a heat exchanger and a flash drum.

8. Method according to any of the preceding claims 3 to 7, wherein the outlet stream comprises solvent, catalyst, dissolved ethylene and linear alpha-olefins.

9. Method according to claim 8, wherein the solvent is selected from toluene, benzene and heptane, wherein toluene being preferred.

10. Method according to any of the preceding claims, wherein the deactivated catalyst is separated from the outlet stream.

11. Method according to any of the preceding claims, wherein the residence time of the catalyst-containing outlet stream in the heating device is from about 1 millisecond to about 1 minute.

12. Reactor system for catalyzed processes comprising a reactor and a heating device connected thereto to heat a catalyst-containing outlet stream of the reactor to a temperature of at least 160°C.

13. Reactor system according to claim 12, wherein the heating device is a thin film evaporator or a heat exchanger and a flash drum.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C2/30 C07C2/08 C08F10/02 C07C45/50 B01J19/18

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 C08F B01J

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, PAJ, WPI Data, CHEM ABS 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 5 811 619 A (COMMEREUC ET AL) 22 September 1998 (1998-09-22) column 1, line 39 - column 3, line 27 example 1	1-6, 8-10,12, 13
A	US 2002/147375 A1 (TEMBE GOPAL LAXMAN ET AL) 10 October 2002 (2002-10-10) paragraphs [0001], [0035], [0036]	1-13
A	US 4 486 615 A (LANGER, JR. ET AL) 4 December 1984 (1984-12-04) column 2, line 18 - line 28 column 4, line 17 - line 61	1-13

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 198 07 226 A1 (LINDE AG, 65189 WIESBADEN, DE; INSTITUT OF CHEMICAL PHYSICS IN CHERNOG) 15 October 1998 (1998-10-15) page 3, line 28 - page 4, line 20	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

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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
US 2002147375 A1	10-10-2002	NONE	
US 4486615 A	04-12-1984	NONE	
DE 19807226 A1	15-10-1998	CN 1197783 A	04-11-1998
		RU 2123501 C1	20-12-1998