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(54) Title: CATALYST PASSIVATION METHOD

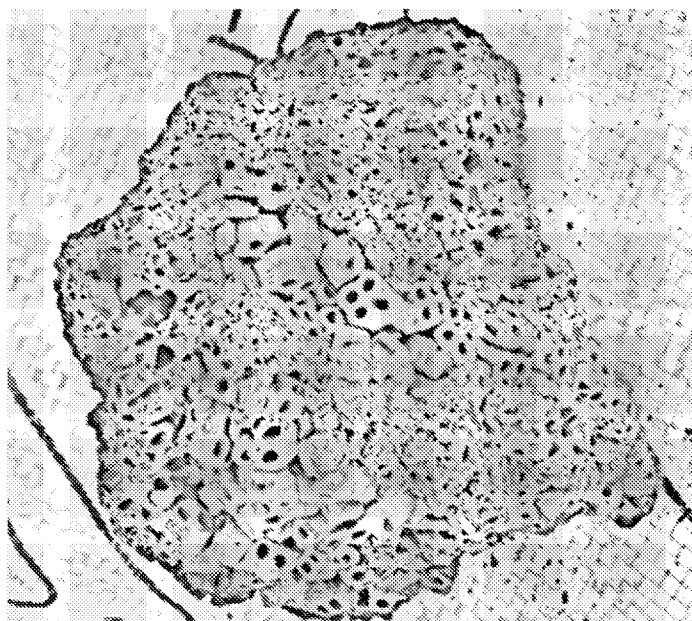


Figure 1.

(57) Abstract: The invention relates to a method of passivating a reduced catalyst, comprising the steps of: (i) carrying out a passivation step by exposing a reduced catalyst to a first gas stream comprising oxygen to produce a passivated catalyst; (ii) carrying out a hydration-passivation step by exposing the passivated catalyst to a second gas stream containing moisture to produce a hydrated-passivated catalyst, wherein the moisture content of the second gas stream is higher than that of the first gas stream; and (iii) discharging the hydrated-passivated catalyst. The invention also relates to catalysts prepared by this method. The reduced catalyst may be a powdered or supported cobalt, copper or nickel catalyst.



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Catalyst passivation method

Field of the Invention

The present invention relates to a method of passivating a catalyst, particularly for passivating a powdered or supported metal catalyst.

5 Background

Reduced catalysts, meaning herein catalysts in which the majority of the metal is in oxidation state 0, are prone to oxidation during discharge from the reactor or subsequent handling or transfer. Uncontrolled oxidation of the catalyst should be avoided because oxidation is an exothermic reaction and an uncontrolled oxidation process can lead to
10 deactivation of the catalyst, for instance due to sintering of metal crystallites. For this reason, catalysts are commonly passivated.

Various methods are known for passivating metal catalysts. One such method is the incorporation of the catalyst into a lipid, which can be achieved by discharging a reduced metal catalyst directly into a molten lipid. Fat encapsulation prevents the catalyst from
15 becoming oxidized following discharge from the reactor and allows for greater ease of handling. An exemplary catalyst employing lipid passivation is PRICAT™ 9910 (Johnson Matthey) which is a powdered Ni catalyst encapsulated in fat and used for the hydrogenation of fatty acids.

However, there are some applications in which fat-encapsulation is not compatible with the
20 end-use of the catalyst. In such applications, a catalyst may be provided in oxidic form and reduced in situ by the user. This has the drawback that appropriate equipment needs to be included in the user's plant to allow the oxidic catalyst to be reduced.

Some manufacturers also offer reduced and passivated (RP) catalysts which have been passivated by partial oxidation of the surface of the metal but do not require the same
25 degree of in situ activation as oxidic catalysts. Typically an RP catalyst is prepared by exposing the reduced catalyst to a gas stream in which the oxygen content of the gas stream is gradually increased up to the oxygen content in air (~21 vol%). The result is a catalyst with a thin layer of metal oxide on its surface. Typically, once this passivation process is complete the catalyst is discharged into the air.

US2677669 (United States Atomic Energy Commission) describes a method of passivation a finely divided pyrophoric metal catalyst by treating the metal catalyst with a circulating gas mixture containing an inert gas and a controlled amount of oxygen. The circulating gas mixture is initially cooled, so that only the most reactive portions of the catalyst are passivated initially. The temperature of the circulating gas is then raised above room temperature at which the less active portions of the catalyst are passivated. This helps to prevent localized overheating.

US2007/078055A1 (Sud-Chemie Catalysts Japan Inc) describes a method of stabilizing a reduced nickel-containing catalyst by contacting the catalyst with a mixed gas composed of O₂, H₂O and CO₂.

The present inventors have noticed that the properties of the resulting RP catalysts are variable, despite careful control of the conditions used during the passivation step. The present invention offers a passivation method which allows for the catalyst to be passivated in a more reliable manner.

Summary of Invention

The present inventors now believe that the reason for the variability in catalyst quality using known conventional passivation routes is because, contrary to the prevalent thinking, controlled exposure of the catalyst to oxygen is not by itself sufficient to produce a passivated catalyst. While oxidation of the surface of the catalyst may be complete following the passivation step, on discharging the catalyst into air the catalyst takes up moisture present in the air. This hydration of the catalyst is an exothermic reaction having the potential to produce local hotspots leading to catalyst deactivation e.g. via sintering. The water content of air is a parameter which is dependent on several factors including temperature and pressure. It is thought that the wide variability in the humidity of air is the reason for the inconsistent degrees of passivation observed previously. In particular, a high absolute humidity is thought to be detrimental to catalyst passivation in the sense that discharging a "passivated" catalyst into an atmosphere having a high absolute humidity has the potential to cause thermal runaway and thereby deactivation of the catalyst. An example of a thermal runaway event is shown in Figure 1.

In a first aspect the invention provides a method of passivating a reduced catalyst, comprising the steps of:

(i) carrying out a passivation step by exposing a reduced catalyst to a first gas stream comprising oxygen to produce a passivated catalyst;

(ii) carrying out a hydration-passivation step by exposing the passivated catalyst to a second gas stream containing moisture to produce a hydrated-passivated catalyst, wherein the moisture content of the second gas stream is higher than that of the first gas stream; and

(iii) discharging the hydrated-passivated catalyst.

In a second aspect the invention provides a catalyst prepared according to the method of the first aspect.

Description of the Figures

Figure 1 is a photograph of an agglomerated mass of catalyst pellets which formed during a runaway reaction during discharge into atmosphere of a supported “passivated” nickel catalyst.

15 Terminology

“Reduced catalyst” means a catalyst in which the majority of the catalytically active metal is in oxidation state 0.

“Passivated catalyst” means a catalyst prepared by exposing a reduced catalyst to an oxygen-containing atmosphere, without subsequently carrying out the hydration step described herein.

“Hydrated-passivated catalyst” means a catalyst prepared by exposing the passivated catalyst to the hydration step described herein.

Detailed Description

Any sub-headings are included for convenience only, and are not to be construed as limiting the disclosure in any way.

Passivation method

In a first aspect the invention provides a method of passivating a reduced catalyst, comprising the steps of:

(i) carrying out a passivation step by exposing a reduced catalyst to a first gas stream comprising oxygen to produce a passivated catalyst;

(ii) carrying out a hydration-passivation step by exposing the passivated catalyst to a second gas stream containing moisture to produce a hydrated-passivated catalyst, wherein the moisture content of the second gas stream is higher than that of the first gas stream; and

(iii) discharging the hydrated-passivated catalyst.

The method of the invention is applicable to a wide range of reduced catalysts, including powdered metal catalysts and supported metal catalysts.

In an embodiment the catalyst is a supported catalyst, comprising a metal on a support. Preferably the catalyst comprises cobalt, copper or nickel on a support.

The method is particularly advantageous when applied to powdered metal catalysts, as such catalysts have a greater % by weight of metal and are more prone to exotherms during passivation than supported catalysts. In an embodiment the catalyst is a powdered metal catalyst. The invention offers particularly advantages when applied to the passivation of powdered metal catalysts having a large negative enthalpy of formation for the corresponding metal hydroxide. In a preferred embodiment the catalysts is a powdered cobalt, copper or nickel catalyst. In a preferred embodiment the catalyst is a powdered nickel catalyst comprising at least 80 wt% nickel.

Step (i)

In this step the reduced catalyst is exposed to a first gas stream comprising oxygen. The vessel used for carrying out passivation steps (i) and (ii) is referred to herein as a passivator. Typically the vessel used to reduce the catalyst and passivate the catalyst will be one and the same.

Typically the first gas stream is provided by a mixture of oxygen and an inert carrier gas such as N₂ or a noble gas such as argon.

Preferably, the oxygen content of the first gas stream is gradually increased during the passivation step until the oxygen content matches that in air (i.e. 21 vol% oxygen). In a preferred embodiment step (i) is carried out by exposing the reduced catalyst to a gas stream initially having an oxygen content of 0.1 to 1 vol% oxygen, preferably 0.1-0.5 vol% oxygen. It is preferred that the oxygen content of the first gas stream is increased gradually during step (i). This helps to avoid exotherms during step (i).

Exotherms can be avoided by monitoring the temperature of the catalyst and adjusting the gas flow and/or oxygen content of the first gas stream accordingly. The skilled person will readily be able to select appropriate conditions and will appreciate that the temperature which can be tolerated without deactivating the catalyst may depend on the choice of metal within the catalyst, whether the catalyst is supported, and so on. In the case of powdered Ni catalysts, it is preferred that the process is controlled such that the temperature of the catalyst is kept below 40 °C. The catalyst is generally assumed to be fully passivated once the oxygen content of the first gas stream is 21 vol% oxygen and the temperature of the catalyst is stable.

It is important that the moisture content of the first gas stream is controlled. Typically, passivation steps are carried out using a “dry” gas stream, in which the H₂O content of the gas stream is in the ppm range, e.g. a water content of less than 100 parts per million volume (ppmv), preferably less than 50 ppmv, preferably less than 20 ppmv, preferably less than 10 ppmv, preferably less than 5 ppmv.

Step (ii)

In a conventional passivation process the catalyst would be discharged from the reactor into the air following completion of step (i). However, the present inventors have found that the catalyst can be produced in a more reliable quality if a controlled hydration step is introduced following step (i) and prior to discharging the catalyst from the reactor.

In step (ii) the passivated catalyst from step (i) is exposed to a second gas stream having a moisture content higher than that of the first gas stream. By this, it is meant that the moisture content of the second gas stream during at least part of step (ii), preferably during all of step (ii), is higher than the moisture content of the first gas stream at any time during step (i).

The moisture content of the second gas stream can be controlled by several methods which will be known to those skilled in the art. A preferred method is a split-stream method. In this method a partially saturated stream is prepared by bubbling a gas through a water bubbler.

- 5 The partially saturated stream is combined with a dry gas stream to produce the second gas stream which is fed to the catalyst in the passivator. The content of the second gas stream will typically be monitored by a hygrometer installed on the gas inlet to the passivator. The moisture content of the second gas stream can be controlled by varying the ratio in which the dry gas stream and partially saturated stream are combined.

10

The carrier for the dry gas stream may be an inert gas such as nitrogen or a noble gas such as Argon. Alternatively, the carrier may be dry air.

Typically, the absolute humidity of the second gas stream is ≤ 0.020 kg H₂O / kg gas.

- 15 Preferably, ≤ 0.014 kg H₂O / kg gas, more preferably ≤ 0.010 kg H₂O / kg gas, more preferably ≤ 0.008 kg H₂O / kg gas. Most preferably the humidity of the second gas stream is ≤ 0.006 kg H₂O / kg gas.

Typically the absolute humidity of the second gas stream will be at least 0.001 kg H₂O / kg gas. Preferred ranges are therefore 0.001-0.020 kg H₂O / kg gas, preferably 0.001-0.014 kg H₂O / kg gas, more preferably 0.001-0.010 kg H₂O / kg gas, more preferably 0.001-0.008 kg H₂O / kg gas. Most preferably the humidity of the second gas stream is 0.001-0.006 kg H₂O / kg gas.

20

- 25 It is preferred that the moisture content of the second gas stream is increased gradually during step (ii). This helps to avoid an exotherm at the beginning of step (ii).

It is preferred that the temperature of the catalyst is monitored during step (ii) and the moisture content of the second gas stream is reduced if the temperature of the catalyst rises too high. In the case of powdered Ni catalysts, it is preferred that the catalyst is kept at a temperature ≤ 30 °C.

30

Step (iii)

In step (iii) the catalyst is discharged from the passivator. Conventionally, catalysts are discharged from the passivator directly into a drum and then blanketed with an inert gas. In the present invention, blanketing with an inert gas may be unnecessary.

- 5 In a second aspect the invention also relates to a catalyst prepared according to a method described herein.

Example

Reduction step

- 10 An oxidic nickel powder (1.4 kg) was charged into a reactor vessel (passivator). The powder was fluidized with N₂ maintaining ≥ 6.3 cm/s. At a gas velocity of 10 cm/s the bed had a depth of ~ 54 cm. A blowback pressure of 2.5 barg N₂ was applied. The passivator was heated by means of a sand bath to 110 °C. The fluidizing N₂ stream was replaced with a H₂ stream and the temperature was increased gradually to 430 °C via the sand bath and held at this temperature until no more water was evolved. The reactor was then cooled down
15 and the fluidizing gas switched from H₂ to N₂.

Passivation step

Initially using 100% N₂ as the fluidizing gas and a gas velocity of 10 cm/s, the content of O₂ in the fluidizing gas was increased gradually to 20% v/v, maintaining the temperature in the reactor below 40 °C throughout. The catalyst was then fluidized with air for ~ 1 h.

- 20 *Hydration-passivation step*

- The humidity of the air stream was increased by bubbling air through distilled water inside a bubbler via a bypass. Control of water addition was achieved by a split stream method, combining a dry air stream and a partially saturated stream which had been passed through a water bubbler. A hygrometer was installed on the gas inlet for the hydration-passivation
25 step. The dew point was controlled to be under 5 °C. Once the temperature was stable and not increasing the passivator was defluidized and the catalyst discharged from the reactor.

Claims

1. A method of passivating a reduced catalyst, comprising the steps of:
 - (i) carrying out a passivation step by exposing a reduced catalyst to a first gas stream comprising oxygen to produce a passivated catalyst;
 - 5 (ii) carrying out a hydration-passivation step by exposing the passivated catalyst to a second gas stream containing moisture to produce a hydrated-passivated catalyst, wherein the moisture content of the second gas stream is higher than that of the first gas stream; and
 - (iii) discharging the hydrated-passivated catalyst.
- 10 2. A method according to claim 1, wherein the reduced catalyst is a powdered metal catalyst.
3. A method according to claim 1 or claim 2, wherein the reduced catalyst is selected from a powdered cobalt catalyst, a powdered copper catalyst or a powdered
15 nickel catalyst.
4. A method according to claim 1, wherein the reduced catalyst is a supported catalyst.
- 20 5. A method according to claim 4, wherein the reduced catalyst comprises cobalt, copper or nickel on a support.
6. A method according to any of claims 1 to 5, wherein the oxygen content of the first gas stream is increased gradually during step (ii).
25
7. A method according to any of claims 1 to 6, wherein the H₂O content of the first gas stream is ≤ 10 ppmv.
8. A method according to any of claims 1 to 7, wherein the absolute humidity of the
30 second gas stream is ≤ 0.020 kg H₂O / kg gas.
9. A method according to any of claims 1 to 8, wherein the absolute humidity of the second gas stream is ≤ 0.010 kg H₂O / kg gas.

10. A method according to any of claims 1 to 9, wherein the moisture content of the second gas stream is 0.001 to 0.020 kg H₂O / kg gas.

5 11. A method according to any of claims 1 to 10, wherein the moisture content of the second gas stream is 0.001 to 0.010 kg H₂O / kg gas.

12. A method according to any of claims 1 to 11, wherein the moisture content of the second gas stream is increased gradually during step (ii).

10

13. A method according to any of claims 1 to 12, wherein the moisture content of the second gas stream fed to the catalyst in step (ii) is monitored using a hygrometer.

14. A method according to any of claims 1 to 13, wherein the second gas stream is
15 provided by moisture in a carrier gas of nitrogen or a noble gas.

15. A method according to any of claims 1 to 13, wherein the second gas stream is provided by moisture in a carrier gas of dry air.

20 16. A method according to any of claims 1 to 15, wherein the moisture content of the second gas stream is controlled using a split-stream method.

17. A catalyst prepared according to the method of any of claims 1 to 16.

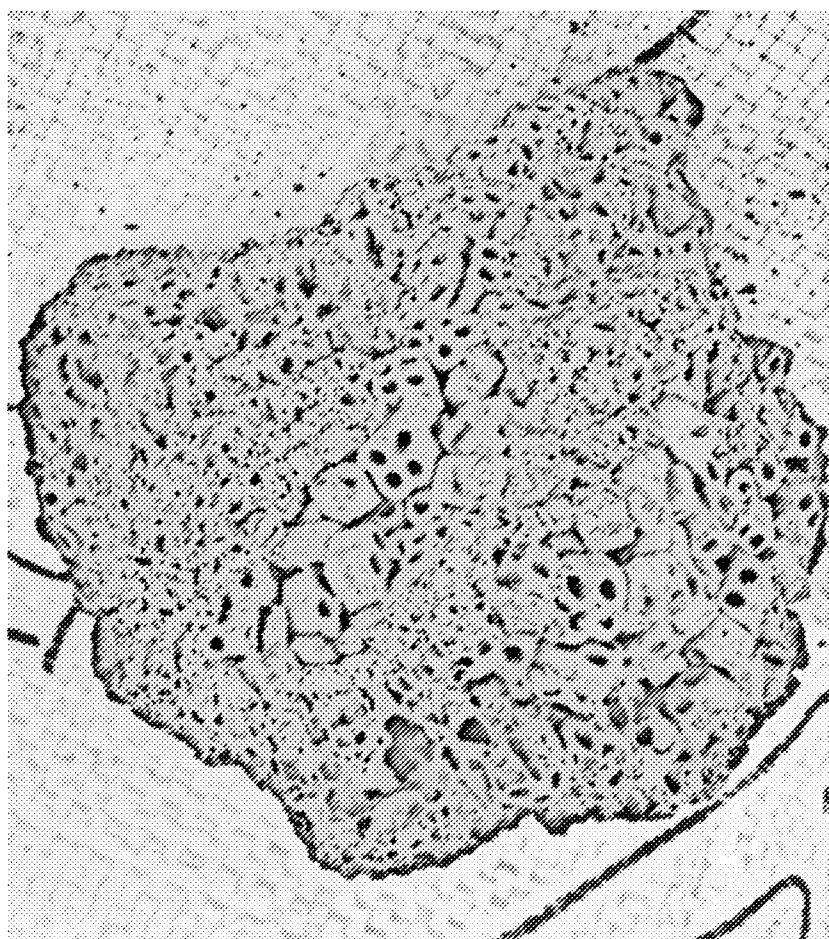


Figure 1.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2022/050001

A. CLASSIFICATION OF SUBJECT MATTER INV. B01J33/00 B01J23/755 B01J23/75 B01J23/72 B01J37/14 B01J37/18 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 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.
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☐ 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 11 April 2022		Date of mailing of the international search report 25/04/2022
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 Beckmann, Oliver

INTERNATIONAL SEARCH REPORT

Information on patent family members

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