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(54) Title: OXIDATION CATALYST FOR THE PURIFICATION OF NITROGEN GAS CONTAINING ORGANIC IMPURI-
TIES

(57) Abstract: An oxidation catalyst for the purification of nitrogen gas containing organic impurities. The catalyst comprises sulphated alumina with a sulphate loading of 1-20 percent weight alumina. The sulphated alumina is impregnated with an aqueous solution of a noble metal complex formed with a complexing agent. The noble metal content of the catalyst is 0.1 to 1 percent weight alumina and the surface penetration of the noble metal on the alumina is 100-150 microns. Also a method of preparing the oxidation catalyst by sulphating alumina with a sulphating agent to a sulphate loading of 1- 20 percent weight alumina; drying the alumina at 110-160°C; calcining the alumina at 520-560°C; complexing a noble metal in 0.1 to 1 percent weight alumina with a complexing agent; impregnating the sulphated alumina with an aqueous solution of the noble metal complex; drying the catalyst material at 110-160°C; calcining the catalyst material at 520-560°C; reducing the catalyst material with hydrogen at 470-500°C; and passivating the catalyst material by cooling it down to 25-50°C in an inert atmosphere.

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TITLE OF THE INVENTION

5 Oxidation catalyst for the purification of nitrogen gas containing organic impurities

FIELD OF THE INVENTION

This invention relates to an oxidation catalyst for the purification of nitrogen gas containing organic impurities, particularly nitrogen gas containing impurities formed of organic
10 compounds from a polymerization reactor like solid-state polycondensation reactor used for the production of aromatic polyester resins.

This invention also relates to a method for the preparation of an oxidation catalyst for the purification of nitrogen gas containing organic impurities, particularly nitrogen gas containing
15 impurities formed of organic compounds from a polymerization reactor like solid-state polycondensation reactor used for the production of aromatic polyester resins.

BACK GROUND OF THE INVENTION

During polymerization of polymers like aromatic polyester resins such as polyethylene
20 terephthalate (PET) resin in polymerization reactors like solid state polycondensation (SSP) reactor, an inert gas such as nitrogen is run through the reactor to strip the developing polymer of the organic impurities which are generally formed of aldehydes and glycols (acetaldehyde and ethylene glycol in the case of polyethylene terephthalate) and glycol oligomers. The impurities being stripped from the polymers accumulate in the nitrogen gas stream. Generally
25 the impurities are present in the nitrogen gas from a SSP reactor, in quantities, defined as methane equivalent of, up to about 2000-3000 ppm (parts per million) by weight or more. The inert gas from a SSP reactor is purified by oxidation of the organic impurities to CO₂ in an oxidation reactor using oxygen or gas containing oxygen (generally air) in excess of the stoichiometric quantity with regard to the organic impurities. The oxidation reaction is carried
30 out at a temperature between 500 and 600°C by circulating the inert gas stream over a catalyst bed formed of a support coated with platinum or platinum and palladium. The oxidation is controlled so that the gaseous stream at the outlet of the oxidation reactor contains oxygen not in excess of 50-500 ppm. Due to the very high requirement of nitrogen in the polymerization and crystallization units of the SSP reactor, the gas hourly space velocity (GHSV, h⁻¹) of
35 nitrogen in the oxidation reactor is very high. Therefore, the catalyst should oxidize the hydrocarbon impurities at very short contact times. The high oxygen content in the gaseous stream coming out of the oxidation reactor is reduced by subjecting the gaseous stream to a

deoxidation treatment with hydrogen. The gaseous stream is then dried by circulating it on a silica gel molecular sieve or other beds of drying materials so as to eliminate the water stripped from the polymer chips and generated in the oxidation and deoxidation stages before being recycled to the SSP reactor.

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Guido et al in US 5547652 teaches a process for the purification of recycle inert gas stream containing organic impurities and leaving a SSP reactor. Oxygen or oxygen containing gas is added to the gas stream in a stoichiometric quantity with respect to the organic impurities or in such an excess amount that the gas at the outlet of the oxidation reactor contains upto 10 ppm of oxygen. Oxidation is carried out at 250 to 600°C, preferably 250 to 350°C using a catalyst comprising Pt or mixtures of Pt and Pd supported on an inert porous support. The catalyst is preferably Pt and Pd supported on gamma alumina having a porosity of 0.4-0.6 cm³/g. The stoichiometry of the oxidation reaction is monitored by an oxygen analyzer like zirconia sensor connected to the outlet of the oxidation reactor. The gaseous stream leaving the oxidation reactor is recycled to the SSP reactor after drying to remove water present.

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Guido et al in US 5612011 further teaches a process for the purification of recycle inert gas stream containing organic impurities and leaving a SSP reactor. Oxygen or oxygen containing gas is added to the gas stream containing impurities and the impurities are oxidized in an oxidation reactor using a catalyst comprising Pt or mixtures of Pt and Pd supported on an inert porous support at 250 to 600°C, preferably 250 to 350°C. The quantity of oxygen used is in such an excess that the gas at the outlet of the oxidation reactor contains greater than 10 ppm but less than or equal to 250 ppm of oxygen. Preferably the catalyst comprises Pt and Pd supported on gamma alumina having a porosity of 0.5 – 0.6cm³/g, preferably 0.4 – 0.6cm³/g.

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James et al in US 6749821 teaches a process for the purification of a recycle inert gas stream leaving a polymerization reactor from organic impurities. Oxygen or a gas containing oxygen is added to the gas stream and the organic impurities in the gas stream are oxidized in an oxidization reactor using a catalyst impregnated with a metal including platinum. All of the metal impregnated on the catalyst is in a substantially reduced state, the reduction having carried out in a gas containing hydrogen. The oxidation is carried out at a temperature less than 300°C preferably 250°C using oxygen or gas containing oxygen substantially stoichiometric quantity with respect to the organic impurities such that the gas leaving the oxidation reactor contains no greater than 250 ppm oxygen. The gas leaving the oxidation

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reactor is dried and recycled to the polymerization reactor. The support for the catalyst comprises activated alumina; platinum is dispersed on the surface of the catalyst; and the catalyst includes 0.1 to 2.0 wt% platinum.

5 OBJECTS OF INVENTION

1 An object of the invention is to provide an oxidation catalyst which has improved activity, for the purification of nitrogen gas either generated or recycled containing organic impurities, particularly impurities formed of organic compounds from a polymerization reactor like solid state polycondensation (SSP) reactor used for the production of aromatic polyester resins.

10 Another object of the invention is to provide an oxidation catalyst which reduces the heat requirement of the process for the purification of nitrogen gas either generated or recycled containing organic impurities, particularly impurities formed of organic compounds from a polymerization reactor like solid state polycondensation (SSP) reactor used for the
15 production of aromatic polyester resins.

Another object of the invention is to provide a method for the preparation of an oxidation catalyst for the purification of nitrogen gas either generated or recycled containing organic impurities, particularly impurities formed of organic compounds from a polymerization
20 reactor like solid state polycondensation (SSP) reactor used for the production of aromatic polyester resins, which catalyst has improved activity.

Another object of the invention is to provide a method for the preparation of an oxidation catalyst for the purification of nitrogen gas either generated or recycled containing organic
25 impurities, particularly impurities formed of organic compounds from a polymerization reactor like solid state polycondensation reactor used for the production of aromatic polyester resins, which catalyst reduces the heat requirement of the process for the purification of nitrogen gas containing organic impurities.

30 DETAILED DESCRIPTION OF INVENTION

According to the invention there is provided an oxidation catalyst for the purification of nitrogen gas containing organic impurities, the catalyst comprising sulphated alumina with a sulphate loading of 1 – 20 percent weight alumina, the sulphated alumina being
7 impregnated with an aqueous solution of a noble metal complex formed with a complexing

agent, the noble metal content of the catalyst being 0.1 to 1 percent weight alumina and the surface penetration of the noble metal on the alumina being 100 – 150 microns.

According to the invention there is also provided a method of preparing an oxidation catalyst for the purification of nitrogen gas containing organic impurities, the method comprising the steps of :

- i) sulphating alumina with a sulphating agent to a sulphate loading of 1 - 20 percent weight alumina;
- ii) drying the alumina of step (i) at 110-160°C;
- iii) calcining the alumina of step(ii) at 520-560°C;
- iv) complexing a noble metal in 0.1 to 1 percent weight alumina with a complexing agent;
- v) impregnating the sulphated alumina of step (iii) with an aqueous solution of the noble metal complex obtained by step (iv);
- vi) drying the catalyst material of step (v) at 110 - 160°C;
- vii) calcining the catalyst material of step (vi) at 520 - 560°C;
- viii) reducing the catalyst material of step (vii) with hydrogen at 470 - 500°C; and
- ix) passivating the catalyst material of step (viii) by cooling it down to 25 - 50°C in an inert atmosphere.

The sulphate loading of the alumina is preferably 1 to 10 percent weight alumina and still preferably 2.4 percent weight alumina. Preferably the alumina comprises gamma alumina spheres having average diameter of 3 - 4 mm, apparent bulk density of 0.3 to 1.0 g/cc, surface area of 100 to 500 m²/g, pore volume of 0.1 to 1 cc/g, pore diameter of 20 to 300 Å and crush strength of 6 to 8 kg. Preferably, the noble metal content of the catalyst is 0.5

percent weight alumina. Preferably the surface penetration of the noble metal on the alumina is 100 microns. The noble metal is selected from platinum or platinum group and is preferably platinum. The platinum is obtained from platinum source selected from chloroplatinic acid, ammonium chloroplatinate, bromoplatinic acid, platinum chloride, platinum tetrachloride hydrate, platinum dichlorocarboxyl dichloride or dinitrodiamino platinum and is preferably chloroplatinic acid. The complexing agent is selected from thiomalic acid or thio glycolic acid and is preferably thiomalic acid. The sulphating agent is selected from sulphuric acid or ammonium sulphate and is preferably sulphuric acid. Preferably the noble metal catalyst is complexed with the complexing agent in 0.3 percent weight alumina.

The catalyst of the invention can be advantageously used for purification of nitrogen gas either generated or recycled containing organic impurities particularly impurities formed of organic compounds from a polymerization reactor like solid state polycondensation (SSP) reactor used for the production of aromatic polyester resins. The sulphate species on the alumina provide pathway for the total oxidation of the hydrocarbon which involves the breaking of a C-C bond instead of H-abstraction. The surface sulfate promotes the dissociative adsorption of hydrocarbon on noble metal such as Pt, which results in higher activity for hydrocarbon oxidation. Hydrocarbon chemisorption on Pt/Al₂O₃ is increased by surface sulfates on gamma-alumina. The highly oxidized Pt species are generated during oxidation reaction. The electronegative sulfate (SO₄²⁻) deposit which lies in close proximity to the edge of Pt atoms would withdraw electron density from the Pt atom, conferring on Pt species a higher positive charge. A new catalytic site consisting of adjacent cationic (oxidized Pt species) and anionic (SO₄²⁻) moieties would then develop and facilitate the initial C-H bond activation. An interfacial sulphate species plays a key role in the increased activity of the catalyst and activation of hydrocarbon molecule. Pt sites are required for the activation of oxygen and subsequent oxidation of alkyl species. The complexing agent helps to restrict the penetration of the active metal to the surface of alumina. The catalyst exhibits increased activity correspondingly increasing the polymerization. The catalyst decreases the hydrocarbon light off temperature thereby reducing the heat requirement of the oxidation reaction. The invention is also economical for the above reasons.

The catalyst of the invention may be regenerated in situ by carbon removal using known methods (Indian Patent No 179243).

The following experimental examples are presented as illustration of the invention and are not intended as undue limitations on the generally broad scope of the invention as set out in the claims.

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EXAMPLE I

A 0.057 molar concentration solution of 45 ml of chloroplatinic acid and 0.3 wt % thiomalic acid in deionized water were mixed and stirred for 1 hour in a flask. The solution was aged for 48 hours and adjusted to a volume of 100 ml with deionized water. 100 gms of gamma alumina spheres having average diameter of 3.5 mm, apparent bulk density of 0.42 g/cc, crush strength of 8.0 kg, surface area of 165 m²/g, pore volume of 0.1 cc/g and pore diameter of 100 Å was added into the flask containing the aged chloroplatinic acid complex and mixed thoroughly. The catalyst material was dried at 150°C for 12 hours in an air flowing oven and taken in a quartz glass tube and calcined in a tubular electrical furnace in flowing air at 540°C for 4 hour. The calcined material was reduced in a reduction reactor in hydrogen gas flow at 485°C for 4 hours. The reactor was cooled down to 50°C and the flow was switched from hydrogen to nitrogen for the passivation of the active material. The catalyst had a platinum content of 0.5 wt-%. The distribution of platinum on the alumina surface was about 100 microns deep as found out by EDXA (Energy Dispersive X-ray Analysis)

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EXAMPLE 2

The procedure of Example 1 was followed using 100g sulphated gamma alumina. The sulphation was carried out by soaking the alumina in 200 ml, 1N sulphuric acid solution. After 4 hrs of soaking, the excess liquid was decanted and the solid was dried at 120°C for 12 Hrs and calcined at 540°C for 4 hrs to get sulphated alumina which was mixed with chloroplatinic acid complex and processed further as described in Example 1. The distribution of platinum on the alumina surface was about 100 microns deep as found out by EDXA.

30 EXAMPLE 3

Evaluation of the catalysts of Examples 1 and 2 vis-à-vis the catalyst prepared by the procedure of Example 1 of US 6749821 for hydrocarbon oxidation was carried out in a

continuous flow fixed bed reactor for generating methane and propane oxidation temperature curves as shown in Figs 1 and 2 of the accompanying drawings. Gas hourly space velocity was kept constant at 9000 Hr^{-1} for the reactions. A gas mixture stream of oxygen and methane or propane and nitrogen (as carrier gas) was used. The flow rates of hydrocarbon and oxygen were adjusted as per stoichiometry. Hydrocarbon analyzer analyzed feed mixture inlet composition. Conversions were calculated based on the unconverted hydrocarbon across the catalyst bed at various reactor temperatures. Fig 1 clearly shows that propane oxidation light off temperature of the catalyst of Example 1 and catalyst of US 6749821 is 190°C , whereas that of the catalyst of Example 2 is 170°C which is 20°C less. Light off temperature of catalyst (T_{50} -Value) is defined as the temperature at which 50% conversion of hydrocarbon takes place. The catalyst of the invention improves the light off temperature by 20°C and enhances the catalytic activity throughout. Fig 2 clearly show that the methane light off temperature of catalysts of Examples 1 and 2 is 477°C whereas that of US 6749821 is 495°C . Catalyst of Example 2 of the invention shows increased activity throughout from 400°C onwards as compared to the catalysts of Example 1 and US 6749821.

EXAMPLE 4

Catalysts of Examples 1 and 2 were tested in a pilot reactor with plant process conditions and nitrogen stream from the gas recycle loop of a polymerization reactor. The pilot reactor was a twin parallel reactor, one comprising the catalyst and the other without any catalyst (blank). The catalysts of Examples 1 and 2 were alternated in the said one reactor. The gas stream from the polymerization reactor was passed through both the reactors. Down stream of these reactors had scrubbers to collect the reactor effluent in deionized water for COD (Chemical Oxygen Demand) and TOC (Total Organic Carbon) analysis. The reactor when used with the catalyst of Example 2 showed a conversion of 99% and when used with the catalyst of Example 1 showed conversion of 92%. The evaluation tests were run for a duration of 10 days.

CLAIMS :

1. An oxidation catalyst for the purification of nitrogen gas containing organic impurities, the catalyst comprising sulphated alumina with a sulphate loading of 1 – 20 percent weight alumina, the sulphated alumina being impregnated with an aqueous solution of a noble metal complex formed with a complexing agent, the noble metal content of the catalyst being 0.1 to 1 percent weight alumina and the surface penetration of the noble metal on the alumina being 100 – 150 microns.
2. An oxidation catalyst as claimed in claim 1, wherein the sulphated alumina is with a sulphate loading of 1 – 10 percent weight alumina.
3. An oxidation catalyst as claimed in claim 1, wherein the sulphated alumina is with a sulphate loading of 2.4 percent weight alumina.
4. An oxidation catalyst as claimed in any one of claims 1 to 3, wherein the alumina comprises gamma alumina spheres having average diameter of 3 - 4 mm, apparent bulk density of 0.3 to 1.0 g/cc, surface area of 100 to 500 m²/g, pore volume of 0.1 to 1 cc/g, pore diameter of 20 to 300A and crush strength of 6 to 8 kg.
5. An oxidation catalyst as claimed in any one of claims 1 to 4, wherein the noble metal content of the catalyst is 0.5 percent weight alumina.
6. An oxidation catalyst as claimed in any one of claims 1 to 5, wherein the surface penetration of the noble metal on the alumina is 100 microns.
7. An oxidation catalyst as claimed in any one of claims 1 to 6, wherein the noble metal is platinum.
8. An oxidation catalyst as claimed in claim 7, wherein the platinum is obtained from chloroplatinic acid.
9. An oxidation catalyst as claimed in any one of claims 1 to 7, wherein the complexing agent is thiomalic acid.

10. A method of preparing an oxidation catalyst for the purification of nitrogen gas containing organic impurities, the method comprising the steps of :

- 5 i) sulphating alumina with a sulphating agent to a sulphate loading of 1 - 20 percent weight alumina;
- ii) drying the alumina of step (i) at 110-160°C;
- 10 iii) calcining the alumina of step(ii) at 520-560°C;
- iv) complexing a noble metal in 0.1 to 1 percent weight alumina with a complexing agent;
- 15 v) impregnating the sulphated alumina of step (iii) with an aqueous solution of the noble metal complex obtained by step (iv);
- vi) drying the catalyst material of step (v) at 110 - 160°C;
- 20 vii) calcining the catalyst material of step (vi) at 520 - 560°C;
- viii) reducing the catalyst material of step (vii) with hydrogen at 470 - 500°C; and
- 25 ix) passivating the catalyst material of step (viii) by cooling it down to 25 - 50°C in an inert atmosphere.

11. A method as claimed in claim 10, wherein the sulphation of the alumina is carried out to a sulphate loading of 1 to 10 percent weight alumina or 2.4 percent weight alumina.

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12. A method as claimed in claim 10 or 11, wherein the sulphating agent is sulphuric acid.

13. A method as claimed in any one of claims 10 to 12, wherein the noble metal catalyst is complexed with the complexing agent in 0.3 percent weight alumina.

14. A method as claimed in any one of claims 10 to 13, wherein the surface penetration of the noble metal on the alumina is 100 microns.
- 5 15. A method as claimed in any one of claims 10 to 14, wherein the noble metal is platinum.
16. A method as claimed in claim 15, wherein the platinum is obtained from chloroplatinic acid.
- 10 17. A method as claimed in any one of claims 10 to 16, wherein the complexing agent is thiomalic acid.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER IPC ⁸ : B01J 23/40 (2006.01); B01J 21/04 (2006.01); B01D 53/44 (2006.01) 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) IPC ⁸ : B 01 D, B 01 J 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) EPODOC, WPI		
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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A	US 3932309 A (GRAHAM et al.) 13 January 1976 (13.01.1976) <i>Claims 1&3.</i> --	1,7,8
A	US 4370260 A (KIM) 25 January 1983 (25.01.1983) <i>Claims 1,9&10.</i> --	1,7
A	US 3259589 A (MICHALKO) 5 July 1966 (05.07.1966) <i>Claims 1-7.</i> --	1,7,8
☒ 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		
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