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(71) Applicant (for US only): SHELL OIL COMPANY
[US/US]; P.O. Box 576, Houston, Texas 77001-0576 (US).

(71) Applicant (for all designated States except US): SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V. [NL/NL]; Carel van Bylandtlaan 30, 2596 HR The
Hague (NL).

(72) Inventor: HAMILTON, JR., David Morris; 1811 Rustic
Hills Court, Sugar Land, Texas 77479 (US).

(74) Agent: CARRUTH, James; SHELL OIL COMPANY,
P.O. Box 576, Houston, Texas 77001-0576 (US).

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(54) Title: A PROCESS FOR THE PREPARATION OF ADIPIC ACID

(57) Abstract: A process comprising: a) hydrogenating an aromatic compound comprising an aromatic ring and a substitutable hydrogen atom on said aromatic ring to form optionally substituted cyclohexene; b) contacting the cyclohexene with an oxidant under conditions effective to form cyclohexanone and unreacted cyclohexene; c) separating the cyclohexanone from the unreacted cyclohexene; and d) contacting at least a portion of the cyclohexanone with nitric acid and a conversion catalyst to produce adipic acid and nitrous oxide.



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A PROCESS FOR THE PREPARATION OF ADIPIC ACID

Cross-Reference to Related Application

This application claims the benefit of U.S. Provisional Application No. 62/441999, filed
5 filed on 4 January 2017, which is incorporated herein by reference.

Field of the Invention

The invention relates to a process for the preparation of adipic acid.

Background of the Invention

In recent years there has been an increasing focus on how to decompose nitrous
10 oxide (N_2O), as it is an atmospheric ozone depletion gas (greenhouse gas) approximately
300 times more potent than CO_2 on a per-mass basis. Nitrous oxide will be formed during
the catalytic oxidation of ammonia in connection with nitric acid production and during
oxidation of alcohols and ketones, for instance, in connection with adipic acid production.

Nitrous oxide is a powerful oxidizing agent that is kinetically stable under
15 atmospheric conditions. Being 36% active oxygen by mass, nitrous oxide is one of the
most atom economical and inexpensive oxidants, comparing favorably even to hydrogen
peroxide. Moreover, the transfer of the active oxygen atom to substrate gives harmless
nitrogen gas as the sole by-product. In contrast to oxygen gas, N_2O oxidation pathways are
non-radical, which can lead to higher product selectivity, fewer side products, and reduced
20 risk of thermal runaway. Nitrous oxide is also an industrial waste product; e.g., in adipic
acid manufacture, one mole of N_2O by-product is produced for every mole of desired
adipic acid. To prevent atmosphere emission, thermal or catalytic destruction of this
potentially useful material is often carried out. Constructive utilization of N_2O waste
streams has potential for positive environmental and economic impact.

25 US 2844626 describes a process for the manufacture of adipic acid by the oxidation
of cyclohexanol, cyclohexanone or a mixture of the two with nitric acid. The reaction is an
exothermic reaction that produces adipic acid, N_2O and small amounts of other nitric gases,
mainly NO and NO_2 . These gaseous NO_x species are converted in a subsequent step to
nitric acid; however, the N_2O is lost as by-product waste. The reaction mixture is cooled
30 and the adipic acid crystallizes out.

US 6900358 describes a process for hydroxylating benzene under catalytic
distillation conditions to produce hydroxylated products such as phenol. The process

includes direct hydroxylation of liquid phase benzene with an oxidant and a zeolite catalyst under conditions effective to prevent coke formation on the catalyst.

Summary of the Invention

The invention provides a process comprising: a) hydrogenating an aromatic
5 compound comprising an aromatic ring and a substitutable hydrogen atom on said aromatic ring to form optionally substituted cyclohexene; b) contacting the cyclohexene with an oxidant under conditions effective to form cyclohexanone and unreacted cyclohexene; c) separating the cyclohexanone from the unreacted cyclohexene; and d) contacting at least a portion of the cyclohexanone with nitric acid and a conversion catalyst to produce adipic
10 acid and nitrous oxide.

Detailed Description of the Invention

The invention provides an improved process for producing adipic acid by recycling the N₂O by-product waste stream to the front end of the adipic acid production process where it is used as a selective oxidant. Recycle of the N₂O by-product waste stream as a
15 process reactant improves adipic acid process economics and reduces the environmental impact of the process as nitrogen, N₂, is the only reaction by-product.

The first step of this process is the hydrogenation of an aromatic compound to form the respective cycloalkene. The aromatic compound may be any aromatic compound with a substitutable hydrogen atom. For example, the aromatic compound may comprise
20 benzene, fluorobenzene, chlorobenzene, toluene, ethylbenzene, and similar compounds.

In one embodiment, when the aromatic compound is benzene, the respective cycloalkene is cyclohexene. This reaction may be carried out in the presence of a catalyst comprising platinum, palladium, ruthenium, rhodium, iridium, rubidium, osmium and mixtures thereof. In another embodiment, the benzene may be hydrogenated in the
25 presence of a metallic nickel hydrogenation catalyst. The catalyst may be a supported catalyst.

The hydrogenation reaction may be carried out at a temperature in the range of from 100 to 230 °C. The hydrogenation reaction may be carried out in any reactor suitable for this reaction, including packed bed reactors, slurry reactors, and shell and tube heat
30 exchange reactors.

The cyclohexene is contacted with an oxidant to produce the respective ketone. Any suitable oxidant may be used, including nitrous oxide, oxygen, air and mixtures thereof. Nitrous oxide is a preferred oxidant. The molar ratio of the oxidant to the

cycloalkene compound is at least about 1:100; preferably 1:10, more preferably 1:3 and most preferably 1:1. In a preferred embodiment, the oxidant to cycloalkene compound ratio is the stoichiometric ratio that will yield the desired product.

This reaction may optionally be carried out in the presence of a porous material to facilitate the intimate mixing of the reactants inside the pores of the porous material. The improved mixing may increase conversion of the cyclohexene, and it may also reduce the formation of by-products caused by local maldistribution of reactants. The porous material is preferably non-catalytic or inert with regards to this oxidation reaction. The porous material may be any suitable porous material, including porous structured or amorphous materials. Structured porous materials generally comprise a channel structure, where the channels have one or more diameters depending on the selected material. In a preferred embodiment, the porous materials are molecular sieves with a multi-dimensional channel structure, for example, zeolites.

In a preferred embodiment, the porous material is selected from the group consisting of MFI, MEL, MTT, MRE, TON, MWW and MTW zeolites. In a more preferred embodiment, the porous material is ZSM-5, ZSM-11, MCM-22, MCM-36, MCM-56, ZSM-12, silicalite-1 or silicalite-2.

This reaction may optionally be carried out in the presence of an oxidation catalyst. Suitable oxidation catalysts are any that will catalyze the oxidation of a cycloalkene compound in the presence of an oxidant. These catalysts include molecular sieves, including zeolites and non-zeolite materials. The zeolite catalyst may have any of the following structures: MFI, MEL, FER, FAU, BEA, MFS, NES, MOR, CHA, MTT, MWW, EUO, OFF, MTW, ITQ-1, ITQ-2, MCM-56, MCM-49, ZSM-48, SSZ-35, or SSZ-39. Preferred zeolite catalysts are modified zeolites, preferably of the MFI structural type, most preferably ZSM-5, ZSM-11 or beta zeolite. The zeolite catalyst preferably comprises one or more metals selected from the group consisting of ruthenium, rhodium, iron, magnesium, cobalt, copper, titanium, rhenium and iridium. The metal may be present in an amount of from 0.01 to 1.5 wt%, preferably in an amount of from 0.1 to 0.5 wt%.

Preferred non-zeolite molecular sieves are aluminum phosphates (AlPO's) or silica aluminum phosphates (SAPO's). These non-zeolites preferably comprise metals, for example, cobalt, vanadium, manganese, magnesium or iron. The catalyst may consist of AlPO's or SAPO's with a fraction of the aluminum or phosphate ions being replaced during synthesis by a transition metal ion. In another embodiment, the transition metal

may be incorporated into the framework of the catalyst after synthesis using known means including ion exchange, impregnation, co-mulling, and physical admixing. Another suitable type of non-zeolite catalyst includes vanadium-peroxide complexes formed by using hydroquinones to produce peroxide species which are transferred to the vanadium complexes.

The reaction may be carried out under catalytic distillation conditions. A portion of the cycloalkene compound is maintained in a liquid phase and the reaction is carried out to manage the heat generated by the exothermic oxidation reaction. The reflux of the unreacted cycloalkene compound makes the reaction substantially isothermal.

The catalytic distillation reactor preferably provides both catalytic zones and distillation zones. The catalytic zone is defined as the portion of the reactor containing the catalyst where the oxidant and cyclohexene compound react to form cyclohexanone. The distillation zone, also called the fractionation zone is defined as the portion of the reactor adapted to separate the cyclohexanone product from the unreacted cyclohexene compound. The distillation zone is a conventional fractionation column design, preferably integral with and downstream of the reaction zone. In another embodiment, the distillation zone may be a separate column. The catalytic distillation reactor can be configured as an up flow reactor, a down flow reactor or a horizontal flow reactor.

In a preferred embodiment, the catalytic zone and the distillation zone are in a single column. The catalytic zone contains an amount of catalyst and the distillation zone contains a number of conventional separation trays. The cyclohexene compound is preferably delivered to the column above the catalyst and the oxidant is fed to the column below the catalyst. Any unreacted cyclohexene compound is either withdrawn from the column once it leaves the catalytic zone, preferably as a vapor, and supplied as makeup or allowed to reflux. The overhead is withdrawn from the column above the catalytic zone and typically will contain a mixture of oxidant and a small amount of cyclohexene compound. The oxidant is preferably separated from the cyclohexene compound by conventional means and recycled as makeup.

During the catalytic distillation, the oxidation reaction occurs simultaneously with the distillation, and the cyclohexanone product is removed from the catalytic zone as it is formed. Removal of the cyclohexanone product minimizes side reactions and decomposition of the cyclohexanone product. The temperature and pressure of the distillation zone of the reactor is controlled to keep any unreacted cyclohexene compound

that travels from the catalytic zone to the distillation zone in the vapor phase, preferably at or above the boiling point of the cyclohexene compound at the given pressure. The catalytic zone is maintained at a temperature that is below the boiling point of the cyclohexanone product. The unreacted cyclohexene compound eventually reaches a point
5 in the reactor where it boils, and, as a result, the temperature of the reactor is controlled by the boiling point of the cyclohexene compound at the system pressure. The exothermic heat of the oxidation reaction will vaporize a portion of the unreacted liquid cyclohexene compound but will not increase the temperature in the reactor. The oxidation reaction has an increased driving force because the cyclohexanone product is removed and cannot
10 contribute to a reverse reaction.

In one embodiment, a cyclohexene compound is oxidized using catalytic distillation to form a cyclohexanone product having a higher boiling point than the cyclohexene compound. The oxidation reaction is catalyzed by an oxidation catalyst in the presence of an oxidant in a catalytic distillation reactor at conditions that also result in fractional
15 distillation.

The oxidant preferably remains in a gaseous state and unreacted oxidant is withdrawn as overhead. The unreacted cyclohexene compound may be allowed to reflux or it may be withdrawn from the distillation zone and added to the original cyclohexene compound feed as makeup.

20 In the catalytic distillation reactor, there is a liquid phase, or internal reflux, and a vapor phase. The liquid phase is denser than the gas phase and it allows for a more dense concentration of molecules for reaction over the catalyst. The fractionation or distillation separates the cyclohexanone product from unreacted materials, providing the benefits of a combined liquid phase and vapor phase system while avoiding continual contact between
25 the catalyst, the reactants and the products

In a preferred embodiment, the catalytic distillation is carried out in a catalytic distillation reactor at a temperature and pressure effective to oxidize the cyclohexene while fractionating or removing the cyclohexanone product from the oxidant and unreacted cyclohexene. The temperature in the distillation zone of the reactor is higher than the
30 temperature in the catalytic zone of the reactor, creating a temperature gradient within the reactor of from about 50 °C to about 400 °C, preferably from about 80 °C to about 300 °C such that the lower boiling components are vaporized and migrate toward the upper portion of the reactor while the higher boiling components migrate toward the lower portion of the

reactor. The temperature in the lower portion of the reactor preferably is higher than the boiling point of cyclohexene but lower than the boiling point of the cyclohexanone product to achieve an effective separation of the cyclohexanone product from the cyclohexene.

The pressure in the reactor is from about 20 kPa to about 5.1 MPa, preferably from about
5 50 kPa to about 3 MPa.

The cyclohexene may be added at any point in the reactor, for example, it may be added to the fixed bed catalyst or to the reflux as makeup. At least a portion of the cyclohexene, preferably from about 10% to about 100%, is fed to the reactor in a liquid state. The oxidant is preferably a gas, and is fed to the reactor at a point below the catalyst
10 bed allowing the oxidant to flow upward into the catalyst bed where the oxidant contacts and reacts with the cyclohexene. Once in the reactor, the cyclohexene contacts the catalyst and the oxidant and the cyclohexene is oxidized to form cyclohexanone. Cyclohexanone has a higher boiling point (156 °C) than cyclohexene (83 °C) which allows for easy separation by fractional distillation.

The overhead taken from the distillation column preferably is partially condensed to separate the unreacted cyclohexene from the unreacted oxidant. The partially condensed overheads are passed to an accumulator where cyclohexene is collected and the gaseous oxidant is taken off. The cyclohexene and the oxidant can be fed back to the distillation column. The heat generated by the oxidation reaction is removed from the reactor by the
20 reflux of unreacted organic compounds, allowing for isothermal operation of the system.

The cyclohexanone is converted to adipic acid by contacting the cyclohexanone with nitric acid in the presence of a conversion catalyst. The reaction is exothermic and occurs with the evolution of nitric and nitrous oxides and carbon dioxide. The reaction products are cooled and the adipic acid which crystallizes out can be filtered or
25 centrifuged. The adipic acid can then be purified as needed.

Suitable conversion catalysts include catalysts comprising one or more of the following metals: vanadium, manganese, copper, cobalt, molybdenum, nickel, lead, chromium, iron and mercury. The conversion catalyst may comprise an oxide, nitrate or acetate of one or more of the metals listed. In another embodiment, the catalyst may
30 comprise vanadium pentoxide.

In one embodiment, the nitrous oxide produced in the cyclohexanone conversion step can be recycled as an oxidant to the step of oxidizing the cyclohexene. The nitric oxide components may be removed from the nitrous oxide by contacting the nitrous and

nitric oxides with ammonia and a Selective Catalytic Reduction (SCR) deNO_x catalyst. In another embodiment, the nitric oxides may be converted to nitric acid which can be recycled to the cyclohexanone conversion step.

In the embodiment where the nitrous oxide is recycled to the cyclohexene oxidation
5 step, additional nitrous oxide may be added to the recycled nitrous oxide stream.

CLAIMS

1. A process comprising:
 - a. hydrogenating an aromatic compound comprising an aromatic ring and a substitutable hydrogen atom on said aromatic ring to form optionally substituted cyclohexene;
 - b. contacting the cyclohexene with an oxidant under conditions effective to form cyclohexanone and unreacted cyclohexene;
 - c. separating the cyclohexanone from the unreacted cyclohexene; and
 - d. contacting at least a portion of the cyclohexanone with nitric acid and a conversion catalyst to produce adipic acid and nitrous oxide.
2. The process of claim 1 wherein the separating of step c) comprises fractional distillation.
3. The process of any of claims 1-2 wherein steps b) and c) are carried out in a catalytic distillation column.
4. The process of any of claims 1-3 wherein the aromatic compound is benzene.
5. The process of any of claims 1-4 wherein the oxidant comprises nitrous oxide, oxygen, air or mixtures thereof.
6. The process of any of claims 1-5 wherein the conditions comprise a temperature of from about 50 °C to about 288 °C.
7. The process of any of claims 1-6 wherein step b) is conducted in the presence of a porous material.
8. The process of claim 7 wherein the porous material comprises silicalite.
9. The process of any of claims 1-8 wherein step b) is conducted in the presence of an oxidation catalyst.
10. The process of claim 9 wherein the oxidation catalyst is a molecular sieve comprising zeolite or non-zeolite materials.
11. The process of claim 10 wherein the oxidation catalyst comprises a zeolite having one or more of the following structures: MFI, MEL, FER, FAU, BEA, MFS, NES, MOR, CHA, MTT, MWW, EUO, OFF, MTW, ITQ-1, ITQ-2, MCM-56, MCM-49, ZSM-48, SSZ-35, SSZ-39
12. The process of claim 11 wherein the oxidation catalyst comprises at least one metal selected from the group consisting of ruthenium, rhodium, iron, magnesium, cobalt, copper, rhenium, titanium and iridium.

13. The process of claim 10 wherein the oxidation catalyst comprises aluminum phosphates (AlPO) or silica aluminum phosphates (SAPO).
14. The process of claim 13 wherein the oxidation catalyst comprises at least one metal selected from cobalt, vanadium, manganese, magnesium, copper, titanium, rhenium and iron.
15. The process of claim 10 wherein the oxidation catalyst comprises a vanadium-peroxide complex.
16. The process of any of claims 1-15 further comprising removing NO_x compounds from the nitrous oxide to form a purified nitrous oxide stream.
17. The process of claim 16 wherein the NO_x compounds are removed from the nitrous oxide stream utilizing a selective catalytic reduction process to form a purified nitrous oxide stream.
18. The process of any of claims 16-17 further comprising passing at least a portion of the purified nitrous oxide stream to step a) for use as an oxidant.
19. The process of claim 18 further comprising adding additional nitrous oxide to the purified nitrous oxide stream before passing it to step a).
20. The process of any of claims 1-19 wherein the conversion catalyst comprises a metal selected from the group consisting of vanadium, manganese, copper, cobalt, molybdenum, nickel, lead, chromium, iron and mercury.
21. The process of claim 20 wherein the conversion catalyst comprises an oxide, nitrate or acetate of one or more of the metals listed.
22. The process of any of claims 1-21 wherein the conversion catalyst is a vanadium pentoxide.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/012020

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C45/28 C07C5/11 C07C51/31 C07C13/20 C07C49/403
C07C55/14

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 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	STIJN VAN DE VYVER ET AL: "Emerging catalytic processes for the production of adipic acid", CATALYSIS SCIENCE & TECHNOLOGY, vol. 3, no. 6, 1 January 2013 (2013-01-01), pages 1465-1479, XP55456074, United Kingdom ISSN: 2044-4753, DOI: 10.1039/C3CY20728E the whole document	1-17, 20-22
A	US 2 844 626 A (JONAS KAMLET) 22 July 1958 (1958-07-22) cited in the application the whole document	1
A	US 2001/044559 A1 (HAMILTON DAVID MORRIS [US]) 22 November 2001 (2001-11-22) cited in the application the whole document	1



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

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

Authorized officer

de Nooy, Arjan

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2018/012020

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2844626	A	22-07-1958	FR 1153191 A 03-03-1958 GB 797464 A 02-07-1958 US 2844626 A 22-07-1958
US 2001044559	A1	22-11-2001	AT 257140 T 15-01-2004 AT 258153 T 15-02-2004 AU 6026401 A 12-11-2001 AU 6898501 A 07-11-2001 CN 1429186 A 09-07-2003 CN 1429191 A 09-07-2003 DE 60101679 D1 05-02-2004 DE 60101679 T2 09-12-2004 DE 60101844 D1 26-02-2004 DE 60101844 T2 18-11-2004 EP 1276706 A2 22-01-2003 EP 1276708 A2 22-01-2003 US 6437197 B1 20-08-2002 US 2001044559 A1 22-11-2001 WO 0181275 A2 01-11-2001 WO 0183415 A2 08-11-2001