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Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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(54) **Title**: OXIDATION OF HYDROGEN BROMIDE

(57) **Abstract**: This invention provides a process for forming elemental bromine. The process comprises bringing feeds of a gas comprising hydrogen bromide and a gas comprising molecular oxygen into contact with a catalyst comprising cerium oxide and/or cerium bromide on an inorganic oxide support. The process is characterized in that the catalyst contains cerium in an amount of about 25 wt% to about 75 wt%, expressed as cerium oxide, relative to the total weight of the catalyst, and that the feeds are at a temperature of about 200°C or below during process initiation, with the proviso that when the feeds are at a temperature of about 100°C or below, the feeds are anhydrous during process initiation.

OXIDATION OF HYDROGEN BROMIDE

TECHNICAL FIELD

[0001] This invention relates to oxidation of hydrogen bromide to bromine presence of a catalyst.

BACKGROUND

[0002] Many industrial processes employ bromine, and produce gaseous hy bromide as a by-product. One way to recover the bromine values is to oxid hydrogen bromide to bromine. Several processes for oxidizing hydrogen bron bromine with oxygen are known, and many run at relatively high temperatures overall reaction for the oxidation can be represented as follows.

$$4HBr + O_2 \rightarrow 2\ Br_2 + 2H_2O$$

[0003] These oxidation processes often involve a catalyst. There are several disc of a cerium compound on a support, with a relatively high minimum reaction tempe see U.S. Pat. Nos. 2,536,457 (700°C); 2,163,877 and 3,346,340 (300°C); 3,3 (225°C); and U.S. Pub. No. 2011/015458 (250°C). Various loadings of cerium o support are taught; see U.S. Pat. Nos. 3,353,916 (0.75 to 25 wt% Ce); 3,273,964 (u wt% Ce); and 5,366,949 (0.15 to 15 wt% Ce). Routes to recover bromine from hy bromide that are economical and/or practical on large scales are desired.

SUMMARY OF THE INVENTION

[0004] This invention provides processes for oxidation of hydrogen brom elemental bromine by contact with a catalyst at relatively low tempei Advantageously, conversions greater than 98% have been achieved at thes conditions. In addition, ambient temperatures are suitable when the process is con under anhydrous conditions.

[0005] An embodiment of this invention is a process for forming elemental br The process comprises bringing feeds of a gas comprising hydrogen bromide an comprising molecular oxygen into contact with a catalyst comprising cerium oxide cerium bromide on an inorganic oxide support, characterized in that the catalyst c cerium in an amount of about 25 wt% to about 75 wt%, expressed as cerium relative to the total weight of the catalyst, and that the feeds are at a temperature o

200°C or below during process initiation, with the proviso that when the feeds a temperature of about 100°C or below, the feeds are anhydrous during process initiat

[0006] These and other embodiments and features of this invention will be still apparent from the ensuing description and appended claims.

FURTHER DETAILED DESCRIPTION OF THE INVENTION

[0007] As used throughout this document, the chemical formula "HBr" star hydrogen bromide; the term "bromine" refers to elemental bromine, Br_2, unless oth specified; and the term "molecular oxygen" refers to O_2.

[0008] Throughout this document, the phrase "HBr gas" is used interchangeabl "gas comprising hydrogen bromide", and the phrase "oxygen gas" is used interchan with "gas comprising molecular oxygen".

[0009] The term "process initiation", and the words "initiating" and "initiat reference to the processes of this invention, as used throughout this document, refe period of time from the beginning of the feeds of the gas comprising hydrogen b and the gas comprising molecular oxygen into the reaction zone until an exotherm in the reaction zone. The exotherm is a significant increase in temperature, typic increase of about 50°C or more.

[0010] In the processes of this invention, hydrogen bromide is oxidized by mo oxygen, O_2, to elemental bromine in the presence of a catalyst; water is a by-produc reaction. The components of the process other than the catalyst are normal preferably in the gas phase at least in the reaction zone.

[0011] Hydrogen bromide from various sources can be subjected to the processes invention, and the HBr gas does not need to be pure. Preferably, the HBr gas c about 20 mol% or more HBr, more preferably about 50 mol% or more HBr. preferably, the HBr gas contains about 20 mol% to about 100 mol%, more pre about 50 mol% to about 100 mol% HBr. In some embodiments, it is preferable to r other substances from their admixture with HBr when they are present in large an As long as the impurities present in the HBr gas do not adversely affect the catalys hydrocarbons), the HBr gas can be subjected to the processes of this invention. impurities, such as sulfur-containing compounds, if present in the HBr gas, may aff catalyst, and should be minimized in, or absent from, the HBr gas. Although the H does not need to be anhydrous, in some embodiments, anhydrous HBr gas is preferr

[0012] The oxidant is molecular oxygen. The molecular oxygen can be in a carrier gas or in a mixture of carrier gases. Suitable carrier gases include helium argon, nitrogen, carbon dioxide, and mixtures thereof; air is an example of a mix carrier gases containing molecular oxygen. Molecular oxygen without a carrier preferred.

[0013] Suitable catalysts in the practice of this invention include cerium oxide, bromide, and mixtures thereof, on an inorganic oxide support; cerium oxide is pre Inorganic oxide supports include zirconia, hafnia, alumina, titania, yttria, silica, thoı the like, and mixtures thereof. Preferred supports comprise zirconia; more pref zirconia is the only support material. The amount of cerium oxide and/or cerium b on the support is preferably about 25 to about 75 wt% as cerium oxide relative to tl weight of the catalyst, preferably about 30 wt% to about 70 wt% as cerium oxide preferably about 40 to about 70 wt% cerium oxide, and especially with about 6(wt% as cerium oxide, relative to the total weight of the catalyst. In some pr embodiments, the catalyst is cerium oxide on zirconia, with about 25 to about 7: preferably about 30 to about 70 wt%, more preferably about 40 to about 70 wt% oxide, and especially about 60 to 70 wt% cerium oxide relative to the total weight catalyst.

[0014] As used throughout this document, the phrase "as cerium oxide" refers amount of cerium on the support, where the numerical value is for cerium oxid example, cerium bromide may be used, but the amount of cerium in the catalyst is as the value for cerium oxide.

[0015] The reaction zone is defined as the area where the HBr gas and the oxyg come into contact with the catalyst. Both HBr and Br_2 are known to corrode steel presence of water, so it is recommended and preferred that the reaction zone is cons of other materials, such as quartz or ceramic; glass-lined reactors may also be used.

[0016] The HBr gas and the oxygen gas can be fed in any desired manner. The H and the oxygen gas can be combined at a time before being fed into the reaction the mixture is kept at a relatively low temperature (*e.g.*, about 100°C or l Preferably, the HBr gas and the oxygen gas are fed to the reaction zone separate another preferred feeding method, the HBr gas and the oxygen gas are mixed imme prior to being fed into the reaction zone.

[0017] It is recommended and preferred to feed the HBr gas and the oxygen proportions such that at least the stoichiometric amount of molecular oxygen is pre the reaction zone. When the amount of oxygen gas supplies less than the stoichic amount of molecular oxygen, a decreased conversion of HBr to elemental bror observed. Preferably, the oxygen gas is fed in in an amount such that an excess of ; mol% to about 20 mol%, more preferably about 2 mol% to about 10 mol%, stil preferably about 5 mol% to about 10 mol%, of molecular oxygen over the stoichic amount is present in the reaction zone.

[0018] Feed temperatures refer to both the HBr gas and the oxygen gas. Wh separately, the HBr gas and the oxygen gas are in the desired feed temperature ran HBr gas and the oxygen gas may be at different temperatures, and are preferably same or similar temperatures (*e.g.*, preferably a difference of about 25°C or less preferably a difference of about 10°C or less). When the HBr gas and the oxygen fed as a mixture, it is understood that the feed temperature is for the mixture, whic the desired feed temperature range.

[0019] At least during process initiation, one or both of the HBr gas and the oxyg are preferably at one or more temperatures of about 200°C or below during their f with the proviso that the gas comprising hydrogen bromide and the gas com molecular oxygen are anhydrous when the feed temperature is about 100°C or bel some embodiments, the processes of this invention are initiated with feeds of HBr g the oxygen gas at feed temperatures in the range of about 100°C to about preferably about 100°C to about 175°C, more preferably at about 100°C to about still more preferably at about 100°C to about 125°C, at atmospheric pressure. Anh conditions are not necessary when feeding the HBr gas and the oxygen gas at about or above.

[0020] When operating with the HBr gas and the oxygen gas feeds under anh conditions, the process can be initiated or conducted with the HBr gas and the oxyg feeds at temperatures of about 100°C or below, and the HBr gas and the oxygen ga can be at temperatures as low as ambient temperatures (*e.g.*, about 18°C). Pr temperatures when the process is initiated with the HBr gas and the oxygen ga: under anhydrous conditions are in the range of about 18°C to about 150°C preferably about 50°C to about 110°C, and still more preferably about 50°C tc 100°C.

[0021] Anhydrous conditions mean the absence of water, but it is understoc adventitious amounts of water may be present. In some preferred embodimer processes of this invention are initiated under anhydrous conditions. Initiating a p under anhydrous conditions generally means that the HBr gas and the oxygen g anhydrous during process initiation.

[0022] While the feed temperatures for the HBr gas and the oxygen gas refer period of time before an exotherm occurs in the reaction zone, the HBr gas and oxygen gas can be fed at their feed temperatures after the exotherm occurs, if desire

[0023] The reaction zone or at least a portion thereof can be preheated, although not necessary, because of the exothermicity of the reaction that occurs during the p Preheating is preferred when operating on smaller scales, *e.g.*, laboratory scales. I initiating the feeds of the HBr gas and the oxygen gas, it is recommended and prefe flush an inert gas (*e.g.*, helium, neon, argon, nitrogen, carbon dioxide, or mixtures two or more of these, preferably nitrogen) through the reaction zone during the preh

[0024] Typically, the preheating is for a period of time at a temperature of about or more, preferably about 125°C to about 250°C, more preferably about 125°C to 200°C, to remove water from reaction zone before starting the feeds of HBr gas a oxygen gas into the reaction zone.

[0025] Heating of the reaction zone is generally not required during the processes invention because the oxidation reaction that occurs in these processes is very exotl The magnitude of the exotherm is large enough that heat transfer from the reaction normally needed to keep the reaction zone at the desired temperature, even when th of HBr gas and the oxygen gas are at ambient temperature.

[0026] All of the components in the reaction zone other than the catalyst are nc and preferably in the vapor phase. This means that the reactants, HBr and O_2, as the products, Br_2 and water, are in the vapor phase while in the reaction zone. minimum, water should be in the vapor phase to prevent condensation of water catalyst. Normally, the heat of reaction is sufficient or more than enough to maint temperature in the reaction zone high enough that all or nearly all of the non-c components remain in the vapor phase.

[0027] Residence times in the reaction zone may be quite short (on the order of se because the oxidation reaction that occurs during the process appears to be instant or nearly instantaneous.

[0028] In some more preferred embodiments of this invention, the inorganic support is zirconia, the cerium is about 30 wt% to about 70 wt%, preferably about 4 to about 70 wt%, more preferably about 60 wt% to about 70 wt%, expressed as oxide, relative to the total weight of the catalyst, and the feeds are at a temperature range of about 100°C to about 175°C during process initiation.

[0029] In other more preferred embodiments of this invention, the inorganic support is zirconia, the cerium is about 30 wt% to about 70 wt%, preferably about 4 to about 70 wt%, more preferably about 60 wt% to about 70 wt%, expressed as oxide, relative to the total weight of the catalyst, and the feeds are at a tempera about 100°C or below during process initiation.

[0030] As mentioned above, the processes of this invention produce elemental b and water. The water can be separated from bromine by any convenient mea preferred method is distillation. Another method is to condense the product into a allow it to separate into layers, and draw off the layers separately; the water laye contains some residual elemental bromine, which can be recovered if desired.

[0031] Elemental bromine produced in the processes of this invention can be recy the process from which the HBr emanated, if applicable. Alternatively, the ele bromine can be used in a different process, or stored for later use.

[0032] The following examples are presented for purposes of illustration, and intended to impose limitations on the scope of this invention.

EXAMPLE 1

[0033] Two gas feed lines were connected to separate arms of a mixing "Y", whi connected to a quartz tube reactor. Connected to and downstream from the reactor are jacketed 1-L flasks that are cooled to 5°C, then a condensing column, followe caustic trap (NaOH, aq., 40%).

[0034] Cerium oxide on zirconia (20 g; 69.5 wt% cerium oxide; Actalys®; Rhodi was placed in the quartz tube reactor. The HBr was supplied from a gas cylind molecular oxygen was supplied from a gas cylinder.

[0035] The quartz tube reactor was preheated at 150°C for 60 minutes with a str nitrogen flushing the quartz tube. Several runs of the reaction were carried out wi the HBr and oxygen feeds at the same selected temperature (100°C, 150°C, or 2 HBr was fed into one gas feed line at a rate of 150 sccm (150 cm^3/min.), and oxyg

fed into the other gas feed line at a rate of 50 sccm, and the mixture of HBr and (was fed from the mixing "Y" into the quartz tube reactor. The HBr and oxygen w for 300 minutes. A visible red vapor was seen after only a few seconds of op During the reaction, an exotherm of approximately 50°C, measured at the outer wal reactor, was observed. Br_2 and water were collected in the two 1-L flasks, the conc column, and the caustic trap. The amount of unreacted HBr was determined on s from the caustic trap by acid-base titration. Results are summarized in Table 1.

TABLE 1

Run	Feed temp.	HBr conversion
1	200°C	98.8%
2	150°C	98.4%
3	150°C	97.2%
4	100°C	99.0%

EXAMPLE 2

[0036] Example 1 was repeated, using air instead of pure oxygen; the air was f rate of 200 sccm. In this Example, the amount of bromine carried over to the caus (~20% of the bromine produced) was greater than in Example 1 (3% of the b produced). Results are summarized in Table 2.

TABLE 2

Run	Feed temp.	HBr conversion
A	200°C	97.2%
B	175°C	93.7%

EXAMPLE 3

[0037] Another run was performed as described in Example 1, except that the was cooled to room temperature under a stream of nitrogen, and the reaction was ru the HBr and oxygen feeds at room temperature (21°C). In this 30-second run, a r Br_2, was observed exiting the reactor. The HBr conversion was not determined.

[0038] These Examples show that the processes of this invention yield a high con of HBr to bromine and water, which are easily separated.

[0039] Components referred to by chemical name or formula anywhere specification or claims hereof, whether referred to in the singular or plural, are ide as they exist prior to coming into contact with another substance referred to by ch name or chemical type (*e.g.*, another component, a solvent, or *etc.*). It matters nc chemical changes, transformations and/or reactions, if any, take place in the re mixture or solution as such changes, transformations, and/or reactions are the result of bringing the specified components together under the conditions cal pursuant to this disclosure. Thus the components are identified as ingredients brought together in connection with performing a desired operation or in forming a composition. Also, even though the claims hereinafter may refer to subs components and/or ingredients in the present tense ("comprises", "is", *etc.*), the re is to the substance, component or ingredient as it existed at the time just before it w contacted, blended or mixed with one or more other substances, components ingredients in accordance with the present disclosure. The fact that a sub component or ingredient may have lost its original identity through a chemical reac transformation during the course of contacting, blending or mixing operati conducted in accordance with this disclosure and with ordinary skill of a chemist, of no practical concern.

[0040] The invention may comprise, consist, or consist essentially of the m and/or procedures recited herein.

[0041] As used herein, the term "about" modifying the quantity of an ingredient compositions of the invention or employed in the methods of the invention re variation in the numerical quantity that can occur, for example, through typical me and liquid handling procedures used for making concentrates or use solutions in t world; through inadvertent error in these procedures; through differences manufacture, source, or purity of the ingredients employed to make the composit

carry out the methods; and the like. The term about also encompasses amounts tha due to different equilibrium conditions for a composition resulting from a particula mixture. Whether or not modified by the term "about", the claims include equival the quantities.

[0042] Except as may be expressly otherwise indicated, the article "a" or "an" if used herein is not intended to limit, and should not be construed as limiti description or a claim to a single element to which the article refers. Rather, the arti or "an" if and as used herein is intended to cover one or more such elements, unl text expressly indicates otherwise.

[0043] This invention is susceptible to considerable variation in its practice. Th the foregoing description is not intended to limit, and should not be construed as li the invention to the particular exemplifications presented hereinabove.

CLAIMS:

1. A process for forming elemental bromine, which process cor bringing feeds of

(i) a gas comprising hydrogen bromide and

(ii) a gas comprising molecular oxygen

into contact with a catalyst comprising cerium oxide and/or cerium bromide inorganic oxide support, characterized in that the catalyst contains cerium in an am about 25 wt% to about 75 wt%, expressed as cerium oxide, relative to the total we the catalyst, and that the feeds are at a temperature of about 200°C or below process initiation, with the proviso that when the feeds are at a temperature of about or below, the feeds are anhydrous during process initiation.

2. A process as in Claim 1 wherein the gas comprising hydrogen b contains about 20 mol% or more hydrogen bromide.

3. A process as in Claim 1 or 2 wherein the gas comprising molecular is pure oxygen.

4. A process as in Claim 1 or 2 wherein the gas comprising molecular is air.

5. A process as in any of Claims 1-4 wherein the inorganic oxide sup selected from the group consisting of zirconia, hafnia, alumina, titania, yttria, silica, and mixtures of any two or more thereof.

6. A process as in Claim 1 or 5 wherein the inorganic oxide sup zirconia.

7. A process as in any of Claims 1-6 wherein the cerium is about 30 about 70 wt%, expressed as cerium oxide, relative to the total weight of the catalyst.

8. A process as in any of Claims 1-7 wherein the molecular oxygen i excess of about 1 mol% to about 20 mol% relative to the hydrogen bromide.

9. A process as in any of Claims 1-8 wherein the feeds are at a tempera the range of about 100°C to about 175°C during process initiation.

10. A process as in any of Claims 1-8 wherein the feeds are at a tempera about 100°C or below during process initiation.

11. A process as in any of Claim 1-8 wherein the feeds are at a tempera the range of about 18°C to about 150°C during process initiation.

12. A process as in any of Claim 1-8 wherein the feeds are at a tempera the range of about 50°C to about 110°C during process initiation.

13. A process as in any of Claims 1-12 wherein the gas comprising hy bromide is fed separately from the gas comprising molecular oxygen.

14. A process as in any of Claims 1-13 wherein the gas comprising hy bromide and the gas comprising molecular oxygen are anhydrous.

15. A process as in Claim 1 wherein the inorganic oxide support is zi wherein the cerium is about 30 wt% to about 70 wt%, expressed as cerium oxide, r to the total weight of the catalyst, and wherein the feeds are at a temperature in th of about 100°C to about 175°C during process initiation.

16. A process as in Claim 1 wherein the inorganic oxide support is zi wherein the cerium is about 30 wt% to about 70 wt%, expressed as cerium oxide, r to the total weight of the catalyst, and wherein the feeds are at a temperature o 100°C or below during process initiation.

17. A process as in Claim 15 or 16 wherein the cerium is about 40 about 70 wt%, expressed as cerium oxide, relative to the total weight of the catalyst.

18. A process as in Claim 15 or 16 wherein the cerium is about 60 about 70 wt%, expressed as cerium oxide, relative to the total weight of the catalyst.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/012579

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B7/09
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)
C01B

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	US 3 310 380 A (LESTER GEORGE R) 21 March 1967 (1967-03-21) claims 1,6; figure 1; examples I, IV	1-18
X	US 3 353 916 A (LESTER GEORGE R) 21 November 1967 (1967-11-21) claims 1,3	1,4-7,9, 14-17
X	US 3 346 340 A (LOUVAR CECELIA J ET AL) 10 October 1967 (1967-10-10) examples I,III,IV,VI,IX	1-18
A	US 5 366 949 A (SCHUBERT PAUL F [US]) 22 November 1994 (1994-11-22) the whole document	1-18

☐ 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

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"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	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2016/012579

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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