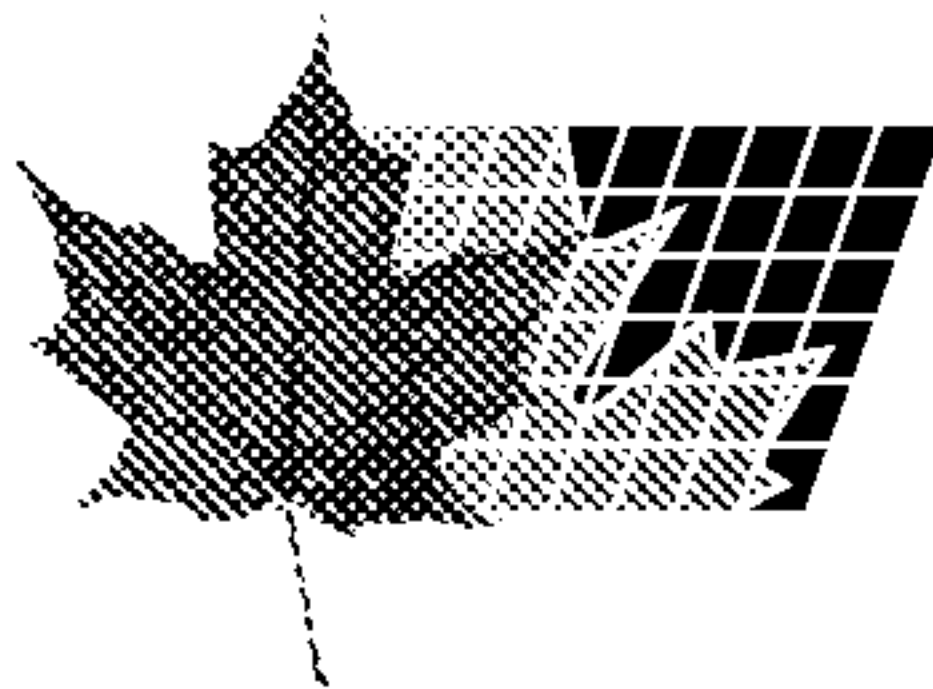




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(54) **PRODUCTION D'UN DIACIDE ALIPHATIQUE ET D'OXYDE
NITREUX**
(54) **METHOD OF PRODUCING AN ALIPHATIC DIACID AND
NITROUS OXIDE**

(57) La présente invention concerne un procédé aboutissant à la production d'un diacide aliphatique et d'oxyde nitreux. L'acide dibasique aliphatique produit résulte de l'oxydation d'un composé aromatique hydrolylé avec de l'oxyde nitreux résultant de la réduction d'un mélange contenant un courant de gaz renfermant un NO_x réutilisé pour la fabrication du diacide aliphatique.

(57) An aliphatic diacid and nitrous oxide are produced by the following methods: the aliphatic dibasic acid is produced by oxidation of an hydrolylated aromatic compound with nitrous oxide to form the aliphatic dibasic acid and the nitrous oxide formed by reducing a mixture of a NO_x containing gas stream and ammonia is employed in the making of the aliphatic diacid.

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METHOD OF PRODUCING AN ALIPHATIC DIACID AND NITROUS OXIDE

FIELD OF THE INVENTION

The present invention relates to the production of nitrous oxide. This invention relates to the use of the nitrous oxide produced for the hydroxylation of aromatic compounds. The invention also relates to the purification of nitrous oxide containing gas streams and subsequent use in the above-mentioned hydroxylation process.

BACKGROUND

Pure nitrous oxide (N_2O) is used as a narcotic gas in medicine, as an oxidizer for various fuels, and as a cleaner in semiconductor production. Recently, nitrous oxide diluted with molecular nitrogen (as mostly available inert gas) has found a new application. It is used as a mild oxidizer to produce various hydroxylated hydrocarbons. However, the technology of this production imposes severe demands on the content of other stronger oxidizers such as oxygen, nitrogen oxide (NO) and nitrogen dioxide (NO_2) that may be present in nitrous oxide as admixtures.

A well known method of nitrous oxide production is by ammonia nitrate (NH_4NO_3) melt decomposition at $220\text{-}250^\circ\text{C}$ (see USSR author license No 1097556). However, this method is difficult to control due to high probability of spontaneous decomposition. Therefore, it is not possible to easily construct units of high capacity, and thus to produce nitrous oxide on a large scale. Moreover, ammonia nitrate is quite expensive, thus increasing nitrous oxide production cost. Furthermore, an additional nitrogen source is required to obtain significant quantities of nitrous oxide diluted with nitrogen.

There are also methods of nitrous oxide production based on selective ammonia (NH_3) oxidation by molecular oxygen (O_2) over various metal oxide catalysts at $200\text{-}500^\circ\text{C}$ under pressure mounting to 20 atm. Since these methods use a less expensive raw material, the product cost is lower. Moreover, the method is safer thus allowing plants of large capacity.

For example, according to a method of nitrous oxide production via selective ammonia oxidation (Japanese Patent Application No. 46-33210), a reaction gas mixture containing ammonia and molecular oxygen passes through a catalyst bed yielding a reaction product gas mixture containing nitrous oxide, nitrogen oxides, water vapor, molecular oxygen and molecular nitrogen. After water condensation on cooling, the gas mixture is divided into two flows. One of the flows returns to the inlet reaction mixture, and the other flow is subject to separation processes to provide

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pure nitrous oxide. Ammonia concentration in the process does not exceed 10-15 vol.% in order to avoid the explosive range of ammonia-oxygen systems. The obtained reaction product gas mixture contains considerable amounts of admixtures such as nitrogen oxide, nitrogen dioxide (e.g., NO_x), and oxygen, which are stronger oxidizers than nitrous oxide and are, thus, not desirable in
5 hydroxylated hydrocarbon production.

In another method (Japanese Patent Application No 6-122505), an inlet reaction gas mixture containing ammonia, molecular oxygen and water vapor passes over or through a catalyst bed to yield a reaction product gas mixture containing nitrous oxide, molecular oxygen, slipped ammonia, molecular nitrogen, nitrogen oxides (NO_x) and water vapor. Ammonia slip and water condense on
10 cooling and return to the inlet reaction mixture. Therefore, there is more than 50 vol.% water vapor in the reaction mixture, which recycles when condensed from the gas phase reaction product. Such a dilution of reaction mixture with water vapor allows a higher selectivity towards nitrous oxide and its higher concentrations in the final product. Water addition also makes the process safer increasing the lower limit of ammonia explosive range.

15 The main disadvantage of the above method is that much energy is spent on the cooling condensation and evaporation of the ammonia solution, thus increasing the production cost of nitrous oxide. Note also that more than 50 vol.% water must be present in the reaction mixture for explosion safety purposes, requiring even more energy for condensation and evaporation. In order to decrease the content of nitrogen oxide admixture in the final product of this process, the
20 oxygen/ammonia volume ratio in the reaction mixture at the inlet of a highly selective CuO-MnO₂ catalyst bed is maintained within 0.5-1.5. When using any other highly selective catalysts, this process does not provide desired results.

U. S. Patents Nos. 5,055,623; 5,001,280; and 5,110,995; the subject matter of which is incorporated herein by reference in its entirety describes the hydroxylation of aromatic compounds
25 to aromatic alcohols (e.g., phenol) utilizing nitrous oxide. However, the cost of nitrous oxide for such hydroxylation is cost prohibitive as compared to existing phenol production technology (e.g., the cumene process as set forth in Kirk-Othmer Encyclopedia of Chemical Technology 3rd Ed., Vol. 17, John Wiley & Sons, 1982, pp. 374-377).

In the production of diacids, waste streams are generated, which contain nitrous oxide,
30 NO_x, CO₂, CO, N₂, low boiling organic compounds, and other gases. Heretofore, the nitrous oxide in diacid waste streams has not been recovered due to the exorbitant costs of nitrous oxide

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separation and purification from the waste streams for applications other than extremely pure nitrous oxide for medical purposes. Currently, nitrous oxide in waste streams is either vented, destroyed or recycled to form nitric acid. Accordingly, the use of nitrous oxide from diacid waste streams, including for hydroxylation of aromatics, has not been previously contemplated.

5 Accordingly, there is a need for a process to produce nitrous oxide on a large scale, economically, safely, and with high yields and conversion rates.

Moreover, there is also need to provide an economic process for commercial production of phenolic compounds while producing other desirable chemical intermediates.

SUMMARY OF THE INVENTION

10 The present invention is a method to produce nitrous oxide while severely limiting the content of nitrogen oxides (NOx) and oxygen in the final nitrous oxide product stream at extremely low energy consumption using ammonia oxidation.

The present invention also relates to a method for recovering and purifying the nitrous oxide present in various NOx containing gas streams by converting NOx to nitrous oxide by
15 ammonia oxidation.

The present invention concerns a method for the production of an aliphatic diacid by:
hydroxylating an aromatic compound in a reactor using nitrous oxide to form a phenolic compound;
reducing the phenolic compound to form a cycloaliphatic ketone and/or alcohol compound;
20 oxidizing the cycloaliphatic ketone and/or alcohol compound to form an aliphatic diacid compound and a nitrous oxide gas stream;
treating the nitrous oxide gas stream to provide a purified nitrous oxide gas stream;
and recycling the purified nitrous oxide gas stream to the reactor.

The present invention also relates to a method for producing nitrous oxide from a NOx
25 containing gas stream by,

feeding a reaction mixture comprising ammonia and the NOx containing gas stream into a reactor; and

oxidizing the ammonia and reducing the NOx to form a nitrous oxide product stream.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention relates to a method for the production of aliphatic diacid (e.g., adipic, glutaric, succinic, oxalic, etc.) comprising, hydroxylating an aromatic compound using nitrous oxide to form a phenolic compound; reducing said phenolic compound to form a cycloaliphatic ketone/alcohol compound oxidizing said cycloaliphatic ketone/alcohol compound to form an aliphatic diacid compound and a nitrous oxide gas stream; treating said nitrous oxide gas stream to provide a purified nitrous oxide gas stream; and recycling said purified nitrous oxide gas stream to said hydroxylating step.

The hydroxylation of aromatic compounds is conducted directly by the oxidation of the aromatic nucleus using nitrous oxide over a zeolite catalyst as is described in U.S. Patents Nos. 5,110,995; 5,672,777; and 5,756,861; the subject matter of which is incorporated herein by reference in its entirety.

For example, a mixture of benzene and nitrous oxide is contacted with a catalyst in a reactor under conditions selected to oxidize the benzene to phenol. The molar ratio of nitrous oxide to benzene in the mixture may be less than 0.5. The ratio of nitrous oxide to benzene may be sufficiently low to provide at least 90 mole percent of the obtainable selectivity of the reaction of benzene to phenol. By "obtainable selectivity" is meant the maximum selectivity of benzene to phenol which can be obtained for given reaction conditions and catalyst by reducing the mole ratio of nitrous oxide to benzene. When preferred catalysts are utilized at normal reaction temperatures, obtainable selectivity is typically approached or attained at a nitrous oxide to benzene ratio of about 0.1. Downstream from the reactor, the unreacted benzene can be separated from the product by conventional separation techniques and recycled to the reactor.

The mixture of nitrous oxide, benzene and any inert gas used in the reactor (the benzene-nitrous oxide reaction mixture) may contain at least 0.3 mole per cent nitrous oxide. Lower amounts tend to restrict productivity. By selecting the proportions of the mixture in the reactor adiabatic temperature rise from the exothermic reaction can be limited to 150 degrees C or less. When this is done the reaction can be carried out adiabatically eliminating the use of costly heat exchange means without unduly increasing formation of undesired by products. Increasing the inert gas or benzene content of the mixture for temperature control also renders the mixture less flammable.

The process will generally be conducted in a temperature range of from 250-600 degrees C. Higher temperatures may result in formation of undesirably high levels of by-products whereas

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lower temperatures may unduly slow the rate of reaction with most catalysts. However, any temperature providing an acceptable reaction rate without excessive by-product formation may be utilized. Any catalyst effective for the partial oxidation of benzene or substituted benzene to phenol or substituted phenol may be utilized. For example, vanadium pentoxide on silica or various zeolites may be employed. Preferred catalysts include acidified ZSM-5 and ZSM-11 containing catalytically effective amounts of iron. Further, productivity of the process can be enhanced by using a zeolite that has been hydrothermally treated by exposure to water vapor in air at about 500-900°C for about 2 hours. Such treatment is described in U.S. Application No. 08/419,361 filed April 10, 1995 and copending herewith, the disclosure of said application being incorporated herein by reference.

In general, the process will be operated to maximize benzene selectivity for phenol (moles of phenol produced per mole of benzene reacted); to maximize nitrous oxide selectivity for phenol (moles of phenol produced per mole of nitrous oxide reacted); to maximize productivity (mass of phenol produced per unit time divided by catalyst mass); and to minimize catalyst activity loss rate. (The yield of nitrous oxide or benzene to phenol will usually be somewhat lower than the selectivity due to material losses in the system.)

The primary reaction to convert benzene to phenol is accompanied by various side reactions including: a reaction converting benzene to coke; a reaction converting benzene to carbon dioxide and carbon monoxide; and a reaction converting benzene to various partially oxygenated aromatics, e.g. dihydroxybenzenes.

It will be recognized that the variables discussed above other than the proportions of feed components are not independent. For example, increasing the feed temperature increases the reactor exit temperature because it increases the reaction rate and nitrous oxide conversion. Also, the average nitrous oxide concentration in the reactor decreases due to higher conversion. The yield of nitrous oxide to phenol will depend on whether the benefit from the lower nitrous oxide concentration is greater or less than the penalty for the higher temperature. Similarly, the productivity will depend on whether any decrease in selectivity is offset by an increase in nitrous oxide conversion.

The phenol obtained in the foregoing reaction is hydrogenated to form a mixture of cyclohexanol and cyclohexanone (generally referred to as KA oil). Reactions of this type are well known as shown in GB Patents Nos. 1,063,357; 1,257,607; 1,316,820; 1,471,854; and U. S. Patents

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Nos. 3,932,514; 3,998,884; 4,053,524; 4,092,360; 4,162,267; 4,164,515; 4,200,553; 4,203,923; 4,283,560; and 4,272,326, the entire subject matter of which is incorporated herein by reference.

In one embodiment, the KA oil is produced by the selective hydrogenation of phenol in the vapor phase and in the presence of a palladium containing catalyst, characterized in that the
5 reaction is carried out at a temperature of between 100 and 200°C and in the presence of a catalyst comprising 0.3 to 5% by weight of palladium on τ -aluminum oxide, said catalyst also containing between 2 and 60% by weight, based on the entire catalyst substance, of an alkaline earth hydroxide.

Catalysts containing calcium hydroxide as an alkaline earth hydroxide have proved
10 particularly effective.

The catalysts to which the invention relates are preferably produced by shaping τ -Al₂O₃ and an alkaline earth oxide together, then impregnating the shaped catalyst pellets or bodies with aqueous palladium chloride solution or palladium nitrate solution, and subsequently reducing them with hydrogen.

15 The process may be carried out continuously, at a reaction temperature of between 120 and 170°C, either at atmospheric pressure or at an excess pressure, in such a way that phenol vapor and hydrogen are passed, in a molar ratio of 1:5 to 1:50, preferably between 1:10 and 1:25, through the catalyst placed in reaction tubes, in which process a throughput of between 0.15 and 0.30 kg of phenol per litre of catalyst per hour is maintained. The reaction product contains 92-96% of
20 cyclohexanone, 2-4% of cyclohexanol and a few per cent of unconverted phenol.

The KA oil obtained above is reacted with nitric acid to form adipic acid. Reactions of this type are known, for example, as shown in U.S. Patents Nos. 4,423,018; 3,758,564; 3,329,712; and 3,186,952, the entire subject matter of which is incorporated herein by reference. Such reactions yield, in addition to the desired adipic acid, nitrous oxide which is recycled to the benzene oxidation
25 reaction. The nitrous oxide obtained in the reaction is often contaminated with more than 10% NO_x by weight. It is found that high levels of NO_x are deleterious to the benzene to phenol reaction process. Therefore, the nitrous oxide recycle fed to the benzene to phenol reaction should not contain more than 2 percent, preferably no more than 1 percent, and more preferably, not more than 0.1 percent by volume NO_x. The desired purity of the recycle stream can be achieved by
30 control of the KA oxidation to minimize NO_x formation and by dilution of the recycle stream with higher purity nitrous oxide. Such techniques may, however, be economically disadvantageous or

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impractical. Therefore, it is preferable to treat the nitrous oxide gas stream from the adipic acid process to lower the NO_x content.

NO_x removal can be accomplished by any known method. Such processes are described for example in U. S. Patents Nos. 3,689,212; 4,507,271; 5,030,436 and Japanese Patent Publications 5-139710; 7-122505; and 6-122507; the entire disclosures of said patents and publications being
5 incorporated herein by reference.

However, the method of this invention described below is particularly preferred. Not only is the method of this invention an excellent and economical method for NO_x removal in general, it also produces additional nitrous oxide needed for the subsequent hydroxylation of benzene to
10 phenol.

For example, the present invention provides direct production of nitrous oxide with a restricted content of nitrogen oxides and oxygen at low energy consumption.

One embodiment of the present invention relates to a method for the production of nitrous oxide by treating a NO_x containing gas stream comprising,

15 feeding a reaction mixture comprising ammonia and the NO_x containing gas stream into a reactor; and

oxidizing the ammonia and reducing the NO_x to form a nitrous oxide product stream.

In one process of the present invention, NO_x removal from NO_x containing gases may be performed separately from nitrous oxide production or it may be performed simultaneously with
20 nitrous oxide production in the same reactor/process as described herein. Additionally, nitrous oxide production may be performed separately from NO_x removal as a stand alone process.

According to one embodiment of the present method, reaction mixture gas flow containing molecular oxygen, molecular nitrogen, ammonia and water vapor is fed into a reactor catalyst bed for ammonia oxidation with oxygen, the catalyst selectivity towards nitrous oxide being not less
25 than 80%. Reaction gas product, produced in the bed, contains mainly nitrous oxide, nitrogen and water vapor. At a temperature higher than that of water condensation (i.e., at 5° to 450°C, preferably 70 to 330°C, and more preferably 90 to 150°C), a portion of the product gas flow (e.g., 25 to 89%) is then separated and returned to the reaction mixture flow. Optionally, the separated gas product flow portion is mixed with air, ammonia and molecular nitrogen so that the content of molecular
30 oxygen stays within 1.0 to 20.0 vol.%, preferably 1.5 to 15.0 vol.%, and more preferably 2.0 to 12.5 vol.% The ratio of ammonia to oxygen volume concentrations is 0.2 to 5.0, preferably 0.5 to 2.0,

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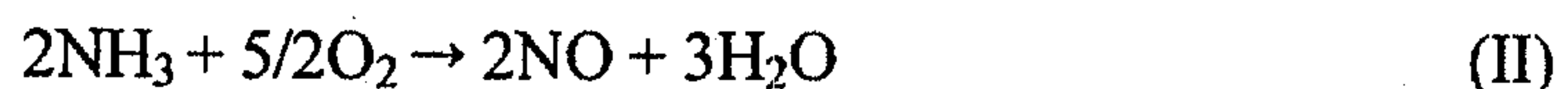
and more preferably 0.8 to 1.5. Nitrous oxide, which may include nitrogen, is produced by separation from the remaining portion of the product gas flow.

In one embodiment, the present method may be performed as follows. First, reaction mixture gas flow is formed in two stages. At the first stage, air cleaned of dust is mixed with the above-mentioned separated and recycled portion of the product gas flow. Then, at the second stage, ammonia is added. Ammonia water may also be used for this purpose (even though ammonia may be added at any of the stages). At one of the stages, nitrogen may be added to obtain a more diluted N₂O gas product. The diluted product may also contain inert admixtures such as CO₂ or argon. The flow rates for air, product portion, ammonia and nitrogen are regulated so that oxygen content in the reaction mixture flow stays within 1.0 to 20.0 vol.%, preferably 1.5 to 15.0 vol.%, and more preferably 2.0 to 12.5 vol.%, while the ratio of volume concentrations of ammonia and molecular oxygen is 0.2 to 5.0, preferably 0.5 to 2.0 and more preferably 0.8 to 1.5.

The reaction mixture gas flow is introduced into a bed of oxidation catalyst. The composition of catalysts for ammonia oxidation to nitrous oxide is MnO₂/Bi₂O₃/Al₂O₃ or MnO₂/Bi₂O₃/Fe₂O₃ or MnO₂ or MnO₂/Bi₂O₃ or MnO₂/CuO. These catalysts provide the following reaction of ammonia oxidation to nitrous oxide:



Simultaneously with reaction (I), undesired reactions occur in the catalyst bed:



Reaction (II) yields nitrogen oxides (NO_x), while reaction (III) decreases the selectivity towards the final product (N₂O). All of the above-mentioned catalysts provide not less than 80% selectivity towards nitrous oxide, which is a key parameter to solve the problem in concern. Meanwhile, only 0.3-3.0% of ammonia is oxidized to NO_x via reaction (II). Partial NO_x reduction occurs on the catalyst via reaction



Ammonia oxidation to nitrous oxide on the catalysts is performed at 200-400°C. Large amounts of heat evolve in the course of reactions (I)-(III). Therefore, heat may be removed to control the reactor temperature. For example, if a tubular reactor (with the catalyst loaded into the tubes) is utilized, or if a multi-bed adiabatic reactor (where the catalyst is organized in beds) is utilized, heat

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may be removed between the beds, or if a fluidized catalyst bed is utilized, with a heat exchanger installed inside the bed.

When passing through the catalyst bed, reaction mixture flow converts to the product gas flow, which contain mainly molecular nitrogen, water vapor, nitrous oxide (N_2O), nitrogen oxides (NOx) as well as residual non-reacted molecular oxygen and ammonia. A portion (1 to 98 vol.%, preferably 10 to 95 vol.%, and more preferably 25 to 89 vol.%) of the product gas flow is then separated at a temperature 5° to 450°C , preferably 70 - 330°C , (and more preferably 90 - 150°C), and returned to the reaction mixture gas flow.

Even though the product gas flow may be condensed prior to recycling, the recycled portion is preferably recycled at a temperature above that of water condensation. This eliminates the need for additional equipment used to condense and vaporize the recycled stream prior to feeding it into the reactor. In such case, the product stream may be condensed subsequent to recycling a portion thereof to the reactor. If the product gas stream is condensed prior to recycling a portion of it to the reactor, any conventional vaporizing means may be used to vaporize the recycled portion, such as the heat obtained from the product stream prior to its condensation, by a conventional heat exchanger, or other heat transfer means. The recycled portion may include N_2O , H_2O , NH_3 , O_2 , NOx and N_2 , etc.

The separated portion of the product gas flow may be continuously recycled to the reaction mixture in two stages. At the first stage, the separated portion of the product gas flow is mixed with continuously supplied air. At the second stage, ammonia is supplied to the gas mixture obtained (although ammonia may be added at any stage). Nitrogen may be added at any stage, and may contain inert admixtures. The reaction mixture gas flow may be prepared so that molecular oxygen content in it stays within 1.0 to 20.0 vol.%, preferably 1.5 to 15.0 vol.%, and more preferably 2.0 to 12.5 vol.%, with the ratio of volume concentrations of ammonia and molecular oxygen ranging within 1.0-1.5.

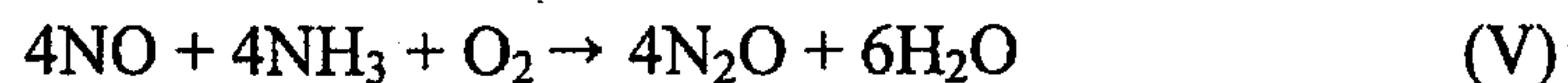
A portion of the product gas flow (5 to 90 vol.%, preferably 8 to 80 vol.% and more preferably 11 to 75 vol.% of the total flow respectively) is withdrawn to provide the final product, namely nitrous oxide, which may be diluted with molecular nitrogen as inert gas. However, to improve the final product constitution, the portion of the product gas flow is passed through a bed of catalyst for selective NOx reduction by ammonia at 150 to 500°C , preferably 175 to 450°C , and more preferably at 200 to 400°C . Reduction catalysts including $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$, $\text{V}_2\text{O}_5/\text{TiO}_2$ or Cr_2O_3

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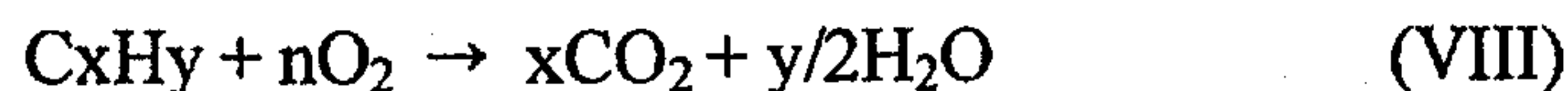
are used for this purpose. Besides reaction (IV), the following reaction proceeds also yielding nitrous oxide:



Reactions (IV) and (V) decrease the content of nitrogen oxide (NO_x), residual oxygen, and
5 ammonia in the final product.

If it is necessary to further decrease more the content of residual oxygen in the final product, gas combustibles (CO, H₂, hydrocarbons) are introduced into the remaining portion of the product gas flow. These combustibles interact with molecular oxygen, yielding only carbon dioxide (CO₂) and/or water. The following reactions proceed:

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For these reactions to occur the product gas flow at a temperature of 50° to 500°C, preferably 175° to 450°C, and more preferably 200° to 400°C is passed through the bed of a deep oxidation catalyst based on metal oxides (MnO₂/Al₂O₃, CuO/Cr₂O₃/Al₂O₃) or noble metals (Pt/Al₂O₃, Pd/Al₂O₃). At the catalyst bed outlet, the N₂O/O₂ ratio is not less than 10, preferably not less than 20, and more preferably not less than 100.

Ammonia and water may be removed from the product gas flow via a known method such as by condensation, etc., and the final product is obtained as a dry gas containing nitrous oxide diluted with molecular nitrogen containing small amounts of admixtures. In case it is necessary to decrease the nitrous oxide concentration in the final product to a certain value, an inert gas, e.g., molecular nitrogen or carbon dioxide, may be introduced into the reaction mixture flow or into the product gas flow.

Another embodiment of the present invention relates to a method for the production of nitrous oxide comprising feeding a reaction mixture comprising ammonia and an oxidant into a reactor; oxidizing the ammonia to form nitrous oxide and NO_x; reducing the NO_x to nitrous oxide and thereby form a nitrous oxide product stream.

The above-mentioned oxidizing step and the reducing step may be performed in one reactor or formed in separate reactors (which, as defined herein, includes separate zones or chambers of one reactor). Additionally, the oxidizing and reducing steps may be conducted simultaneously or in succession using one catalyst or different catalysts. For example, the oxidation catalysts mentioned herein may be utilized or a combination of the oxidation catalysts in one reactor and the reduction catalysts (mentioned herein) in another reactor may be used (under the conditions set forth herein). The reaction product from the reactor may be recycled as set forth herein. Also, when two (or more) reactors are utilized, the products from each reactor may be recycled to the inlet of each reactor, or the reaction product from the last reactor may be recycled to the first reactor.

The oxidant used in the reaction may include oxygen, NO_x, air, ozone, HNO₃ or any oxidant capable of oxidizing ammonia. Preferably, the oxidant is oxygen.

The NO_x present in the reaction product from the first reactor is greater than the NO_x present in the reaction product from the last reactor. The amount of NO_x present in the reaction

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product of the last reactor is less than 5 vol.%, preferably less than 3 vol.% and most preferably, less than 1 vol.% by volume of the reaction product stream.

EXAMPLES

A process of the present invention are further defined by reference to the following
5 illustrative examples.

Example 1

A process for producing nitrous oxide is performed as follows. Air, preliminary cleaned from dust, is added with a rate of 7.32 liter/min to the separated portion of the product gas flow supplied with a rate of 21.0 liter/min. Then ammonia is added to the mixed flow with rate of 1.24
10 g/min. Thus obtained reaction mixture gas flow is continuously fed into a chemical reactor made as a metal tube with an inner diameter of 15 mm, a fixed bed of manganese bismuth catalyst ($\text{MnO}_2/\text{Bi}_2\text{O}_3/\text{Al}_2\text{O}_3$) with a mass of 650 g being inside the tube. The tube with the catalyst is installed inside an air fluidized sand bed providing intensive reaction heat removal. The catalyst bed temperature is maintained at 300°C. The product gas flow, which exits the catalyst bed,
15 contains molecular nitrogen, water, nitrogen oxides (NO and NO_2), residual non-reacted ammonia and oxygen as well as nitrous oxide. At a temperature of 90°C, providing no water condensation a portion of the product gas flow is separated and recycled to the catalyst bed. The remaining portion of the product gas flow is withdrawn from the recycling loop to evolve the final product using already known methods.

20 Under continuous regime with the said supply flow rates reaction mixture gas flow at reactor inlet has the following composition (in vol.%): N_2 - 63.3, H_2O - 19.9, NO - 0.05, N_2O - 5.1, NH_3 - 6.5, O_2 - 4.9. The non-recycled portion of the product gas flow attains 30% of the total product gas flow, and has the following composition (in vol.%): N_2 - 63.8, H_2O - 27.3, NO - 0.07, N_2O - 7.3, NH_3 - 1.5, O_2 - 0.05.

25 Example 2

A process is performed as in example 1. Bulk catalyst $\text{MnO}_2/\text{Bi}_2\text{O}_3$ with a mass of 1200 g is used. Air supply rate is 1.4 liter/min, the separated portion of the product gas flow being supplied with a rate of 13.3 liter/min. Ammonia supply rate is 0.22 g/min. The catalyst bed temperature is 320°C. The separation of the product gas flow portion is performed at 320°C.

30 Under continuous regime with the said supply flow rates reaction mixture gas flow at reactor inlet has the following composition (in vol.%): N_2 - 64.7, H_2O - 24.7, NO - 0.15, N_2O -

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6.47, NH_3 - 2.0, O_2 - 2.0. The non-recycled portion of the product gas flow is 88.7% and has the following composition (in vol.%): N_2 - 64.8, H_2O - 27.5, NO - 0.17, N_2O - 7.29, NH_3 - 0.1, O_2 - 0.15.

Example 3

5 A process is performed as in example 1. Bulk catalyst MnO_2 with a mass of 1550 g is used. Air supply rate is 9.3 liter/min, the separated portion of the product gas flow being supplied with a rate of 3.8 liter/min. Ammonia supply rate is 1.46 g/min. The catalyst bed temperature is 330°C. The separation of the product gas flow portion is performed at 330°C.

Under continuous regime with the said supply flow rates reaction mixture gas flow at
10 reactor inlet has the following composition (in vol.%): N_2 - 64.3, H_2O - 8.7, NO - 0.04, N_2O - 1.68, NH_3 - 12.8, O_2 - 12.5. The non-recycled portion of the product gas flow is 75.0% and has the following composition (in vol.%): N_2 - 65.1, H_2O - 27.4, NO - 0.17, N_2O - 6.66, NH_3 - 0.25, O_2 - 0.47.

Example 4

15 A process is performed as in example 1. Bulk catalyst MnO_2/CuO with a mass of 850 g is used. Air supply rate is 7.27 liter/min, the separated portion of the product gas flow being supplied with a rate of 21.1 liter/min. Ammonia supply rate is 1.30 g/min. The catalyst bed temperature is 310°C. The separation of the product gas flow portion is performed at 70°C.

Under continuous regime with the said supply flow rates reaction mixture gas flow at
20 reactor inlet has the following composition (in vol.%): N_2 - 63.2, H_2O - 19.8, NO - 0.06, N_2O - 4.76, NH_3 - 7.3, O_2 - 4.9. The non-recycled portion of the product gas flow is 30.0% and has the following composition (in vol.%): N_2 - 63.5, H_2O - 27.2, NO - 0.08, N_2O - 6.79, NH_3 - 2.32, O_2 - 0.15.

Example 5

25 A process is performed as in example 1. Catalyst $\text{MnO}_2/\text{Bi}_2\text{O}_3/\text{Fe}_2\text{O}_3$ with a mass of 850 g is used. Air supply rate is 6.32 liter/min, the separated portion of the product gas flow being supplied with a rate of 18.0 liter/min. Ammonia supply rate is 1.02 g/min. Pure nitrogen is added to the reaction mixture flow with a rate of 4.31 l/min. The catalyst bed temperature is 310°C. The separation of the product gas flow portion is performed at 100°C.

30 Under continuous regime with the said supply flow rates reaction mixture gas flow at reactor inlet has the following composition (in vol.%): N_2 - 77.1, H_2O - 11.3, NO - 0.06, N_2O - 2.67, NH_3 - 4.6, O_2 - 4.3. The non-recycled portion of the product gas flow is 40.0%, and has the

following composition (in vol.%): N_2 - 77.3, H_2O - 17.8, NO - 0.11, N_2O - 4.44, NH_3 - 0.30, O_2 - 0.08.

Example 6

A process is performed as in example 1. Catalyst $\text{MnO}_2/\text{Bi}_2\text{O}_3/\text{Al}_2\text{O}_3$ with a mass of 650 g is used. Air supply rate is 6.93 liter/min, the separated portion of the product gas flow being supplied with a rate of 17.1 liter/min. Ammonia supply rate is 1.08 g/min. Inert gas is added to the reaction mixture flow with a rate of 4.51 liter/min containing 90 vol.% of nitrogen and 10 vol.% of CO_2 . The catalyst bed temperature is 310°C . The separation of the product gas flow portion is performed at 100°C .

Under continuous regime with the said supply flow rates reaction mixture gas flow at reactor inlet has the following composition (in vol.%): N_2 - 73.4, H_2O - 10.9, NO - 0.06, N_2O - 2.70, NH_3 - 4.8, O_2 - 4.6, CO_2 - 3.5. The non-recycled portion of the product gas flow is 43.0%, and has the following composition (in vol.%): N_2 - 73.5, H_2O - 17.1, NO - 0.11, N_2O - 4.74, NH_3 - 0.16, O_2 - 0.09, CO_2 - 3.5.

Example 7

A process is performed as in example 1. Catalyst $\text{MnO}_2/\text{Bi}_2\text{O}_3/\text{Al}_2\text{O}_3$ with a mass of 850 g is used. Air supply rate is 4.35 liter/min, the separated portion of the product gas flow being supplied with a rate of 15.9 liter/min. Ammonia is supplied as ammonia water with a 20 wt.% ammonia content by evaporation. Ammonia water supply rate is 3.89 g/min. The catalyst bed temperature is 300°C . The separation of the product gas flow portion is performed at 100°C .

Under continuous regime with the said supply flow rates reaction mixture gas flow at reactor inlet has the following composition (in vol.%): N_2 - 36.6, H_2O - 52.0, NO - 0.06, N_2O - 2.68, NH_3 - 5.1, O_2 - 3.5. The non-recycled portion of the product gas flow is 37.0%, and has the following composition (in vol.%): N_2 - 36.7, H_2O - 57.2, NO - 0.09, N_2O - 4.25, NH_3 - 1.58, O_2 - 0.11.

Example 8

A process is performed as in example 2. The remaining portion of the product gas flow withdrawn for the final product evolution is passed through the bed of a $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst for the nitrogen oxides reduction by ammonia. The catalyst bed temperature is 320°C . Residual NO content after the catalyst bed is 0.005 vol.%.

Example 9

A process is performed as in example 3. Hydrogen with a rate of 0.1 liter/min is added to the remaining portion of the product gas flow, and the mixture is passed through the bed of a Pt/Al₂O₃ catalyst. The catalyst bed temperature is 330°C. Residual O₂ content after the Pt catalyst
5 bed is 0.025 vol.%.

Example 10

A process for producing nitrous oxide is performed as follows. The composition and flow rate of reaction mixture continuously fed into a chemical reactor are the same as in example 1. The process is performed in the chemical reactor consisting of the adiabatic part containing a fixed bed
10 of Fe₂O₃ based catalyst with a mass of 200 g and the cooled tubular part (a tube with an inner diameter of 15 mm containing a fixed bed of manganese bismuth catalyst (MnO₂/Bi₂O₃/Al₂O₃) with a mass of 650 g). The reaction mixture temperature at the inlet of the adiabatic part is 300°C, at the inlet of the tubular part - 280°C. The reaction mixture is cooled down between the adiabatic and tubular parts. In all other respects the process is performed as in example 1. The composition
15 of reactor outlet and recycled gas streams is identical to example 1.

Example 11

A process for producing nitrous oxide is performed as follows. The composition and flow rate of reaction mixture continuously fed into a chemical reactor are the same as in example 1. The chemical reactor is made as a metal tube with an inner diameter of 20 mm, a fixed bed of
20 manganese bismuth catalyst (MnO₂/Bi₂O₃/Al₂O₃) with a mass of 800 g being inside the tube. The tube with the catalyst is installed inside an air fluidized sand bed providing intensive reaction heat removal and kept at the temperature of 280°C. The reaction mixture temperature at the inlet of the reactor is 350°C. In all other respects the process is performed as in example 1. The composition of reactor outlet and recycled gas streams is identical to example 1.

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CLAIMS:

1. A method for the production of an aliphatic diacid comprising:
hydroxylating an aromatic compound in a reactor using nitrous oxide to form a phenolic compound;
5 reducing said phenolic compound to form a cycloaliphatic ketone or alcohol compound;
oxidizing said cycloaliphatic ketone or alcohol compound to form an aliphatic dibasic acid compound and a nitrous oxide gas stream;
treating said nitrous oxide gas stream to provide a purified nitrous oxide gas stream; and
recycling said purified nitrous oxide gas stream to said reactor.
- 10 2. A method according to claim 1, wherein said treating comprises conversion of O₂ to nitrous oxide, and reduction of NO_x to N₂ and nitrous oxide.
3. A method according to claim 2, wherein said conversion of O₂ comprises converting said O₂ to nitrous oxide by ammonia oxidation.
4. A method according to claim 2, wherein said reduction of NO_x comprises ammonia
15 oxidation, which produces nitrous oxide as a reaction product.
5. A method according to claim 1, wherein said purified nitrous oxide gas stream is mixed with additional nitrous oxide.
6. A method according to claim 5, wherein said additional nitrous oxide is produced by ammonia oxidation.
- 20 7. A method according to claim 6, wherein said ammonia oxidation comprises,
feeding a reaction mixture comprising ammonia nitrous oxide and an oxidant into an ammonia oxidation reactor;
oxidizing the ammonia to form a nitrous oxide product stream;
removing at least a portion of said nitrous oxide product stream to form a separate recycle
25 stream;
feeding said separate recycle stream to said ammonia oxidation reactor; and
purifying said nitrous oxide product stream to provide said additional nitrous oxide.
8. A method according to claim 7, wherein said recycle stream comprises a portion of said nitrous oxide product stream, water, air, molecular oxygen, molecular nitrogen, nitrous oxide,
30 NO_x or inert gas.

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9. A method according to claim 7, wherein said recycle stream is removed from said nitrous oxide product stream at a temperature above that of water condensation.
10. A method according to claim 7, wherein air, water, molecular nitrogen, molecular oxygen, nitrous oxide, ammonia or inert gas is added to said recycle stream.
- 5 11. A method for the production of nitrous oxide by treating a NOx containing gas stream comprising,
feeding a reaction mixture comprising ammonia and said NOx containing gas stream into
a reactor; and
reducing the NOx to form a nitrous oxide product stream.
- 10 12. A method according to claim 11 wherein said method comprises,
removing at least a portion of said nitrous oxide product stream to form a separate
recycle stream;
feeding said separate recycle stream to said reactor; and
separating nitrous oxide from said nitrous oxide product stream.
- 15 13. A method according to claim 11, wherein said reaction mixture comprises a diluent comprising a portion of said nitrous oxide product stream, water, air, molecular oxygen, molecular nitrogen, nitrous oxide, or inert gas.
14. A method according to claim 11, wherein air, water, molecular nitrogen, molecular oxygen, nitrous oxide, ammonia or inert gas is added to said recycle stream.
- 20 15. A method for the production of nitrous oxide by ammonia oxidation comprising,
feeding a reaction mixture comprising ammonia and an oxidant into a reactor;
oxidizing said ammonia to form a nitrous oxide product stream comprising nitrous oxide
as the primary component; removing at least a portion of said nitrous oxide
product stream at a temperature above that of water condensation to form a
25 separate recycle stream;
feeding said separate recycle stream to said reactor; and
separating nitrous oxide from said nitrous oxide product stream.
16. A method according to claim 15, wherein said reaction mixture comprises a diluent comprising a portion of said nitrous oxide product stream, water, air, molecular oxygen,
30 molecular nitrogen, nitrous oxide, or inert gas.

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17. A method according to claim 15, wherein air, water, molecular nitrogen, molecular oxygen, nitrous oxide, ammonia or inert gas is added to said recycle stream.
18. A method according to claim 15, wherein said oxidant comprises oxygen, NO_x, air, ozone or HNO₃.
- 5 19. A method for the production of nitrous oxide comprising,
feeding a reaction mixture comprising ammonia and an oxidant into a reactor;
oxidizing said ammonia to form nitrous oxide and NO_x;
reducing said NO_x to nitrous oxide and form a nitrous oxide product stream.
- 10 20. A method according to claim 19, wherein a portion of said nitrous oxide product stream is recycled to said reactor.
21. A method according to claim 19, wherein said oxidizing is conducted in a first reactor to form a first nitrous oxide product stream and said reducing is conducted in a second reactor to form a second nitrous oxide product stream.
- 15 22. A method according to claim 21, wherein said first and second reactors are charged with different catalyst.
23. A method according to claim 21, wherein a portion of said second nitrous oxide product stream is recycled to said first or second reactors.
24. A method according to claim 21, wherein the amount of said nitrous oxide present in said second product stream is greater than the amount of nitrous oxide present in said first product
20 stream.
25. A method according to claim 19, wherein said oxidant comprises oxygen, NO_x, air, ozone or HNO₃.