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(54) **Title**: METHOD FOR PREPARING HYDROXYLAMINE

(57) **Abstract**: The invention relates to a method for preparing hydroxylamine in a continuous process, comprising feeding nitrate and phosphate in an acidic aqueous liquid into a reaction zone and reducing nitrate with hydrogen thereby forming hydroxylamine, wherein the nitrate concentration in the reaction zone is less than 1.0 mol/kg, as determined in the liquid leaving the reaction zone, wherein the molar ratio of nitrate to phosphate in the reaction zone is 0.5 or less, and wherein the molar ratio of ammonia to nitrate is in the range of from 2.2 to 7; a method for preparing an oxime and a method of preparing a lactam comprising said method for preparing hydroxylamine.

METHOD FOR PREPARING HYDROXYLAMINE

The invention relates to a method for preparing hydroxylamine in a continuous process, to a method for preparing oximes, and to a method for preparing lactams.

Hydroxylamine (hereinafter also referred to as "HYAM") is a commonly used reagent in a myriad of organic and inorganic reactions. It is in particular suitable for use in the preparation of oximes, in particular cyclohexanone oxime, which may thereafter be converted into caprolactam via a Beckmann rearrangement. Beckmann rearrangement processes for the preparation of caprolactam are generally known in the art, *e.g.* from Ullmann's Encyclopedia of Industrial Chemistry, for instance the 7th edition (2005), Chapter on Caprolactam (DOI: 10.1002/14356007.a05.031 (Retrieved Feb. 18, 2011). Other oximes of which the preparation using hydroxylamine has been described include cyclododecanone oxime (*e.g.* EP-A 1,329, 448) and butanone oxime.

Methods of preparing hydroxylamine are also commonly known in the art. Further, various patent rights have been published on this subject. GB-A-1,287,303 and US-5,364,609, for example, relate to processes wherein nitrate is reduced in a phosphate buffer solution using molecular hydrogen.

The HPO® cyclohexanone oxime process of DSM (see *e.g.* H.J. Damme, J.T. van Goolen and A.H. de Rooij, Cyclohexanone oxime made without by-product $(NH_4)_2SO_4$, July 10, 1972, Chemical Engineering; pp 54/55 or Ullmann's encyclopedia of industrial chemistry (2005), under the Chapter Caprolactam, p 6/7; DOI: 10.1002/14356007.a05.031 (Retrieved Feb. 18, 2011) makes use of two recycling liquids – an inorganic liquid and an organic liquid – in which several reactions and operations take place. The inorganic liquid, an aqueous phosphoric acid and ammonium nitrate-containing solution, is fed to the hydrogenation reactor, where hydroxylamine is produced. Hydroxylamine is formed via reduction of nitrate ions with hydrogen, which is catalysed by a heterogeneous catalyst (palladium-containing catalyst with carbon as carrier).

Gaseous hydrogen is contacted, in a gas-liquid reactor, with a circulating inorganic liquid containing nitrate ions, together with a buffering acid and the catalyst. The hydrogen containing gas phase is circulated over the bubble column type reactor by a circulation compressor. Fresh hydrogen is fed to the circulation gas, a small amount being withdrawn from the system to maintain a constant hydrogen

pressure. Inert gaseous components in the fresh hydrogen and the produced gaseous by-products N_2 and N_2O are removed via the gas purge.

The gas-liquid suspension is circulated by the Mammoth pump principle from the gassed reactor section, over gas-liquid separators, to the filter candles in the filtration section and via a heat exchanger for the removal of heat of reaction, back to the gassed reactor section.

The inorganic liquid obtained after filtration is then contacted in the oximation section with an organic liquid, being a mixture of toluene and cyclohexanone. Here the cyclohexanone is practically quantitatively converted into cyclohexanone oxime. The obtained cyclohexanone oxime-containing organic phase is distilled to recover the toluene.

The inorganic liquid leaving the oximation section has to be purified thoroughly to protect the catalyst in the hydroxylamine reactor. This is done by extraction with toluene, followed by stripping with steam. In the stripping column the water that is co-produced during the preparation of hydroxylamine and cyclohexanone oxime is also removed. A small amount of ammonia by-product remains in solution, but is prevented from building up by conversion of ammonia into nitrogen in an absorber for a gas mixture of NO and NO_2 (*i.e.* of nitric oxide and nitrogen dioxide; hereinafter also referred to as nitrous gases).

Finally, the consumed amount of nitrate should be compensated. The nitrous gases required therefor are produced in an ammonia combustion unit.

EP1947056A1 describes a method for preparing hydroxylamine by reduction of nitrate with hydrogen gas in the presence of a catalyst in an inorganic process solution containing an acidic buffering agent, as part of a combined hydroxylamine and oximation system. It teaches that such a recycle system can reduce the loss rate of hydroxylamine in the inorganic process solution, and reduce organic impurities.

US2006/0079678A1 describes a process for preparing hydroxylammonium by catalytic reduction of nitrate or nitrogen oxide with hydrogen, as part of a system of producing cyclohexanone oxime. It teaches an improved distillation of the cyclohexanone oxime product stream, involving recycle to the cyclohexanone oxime synthesis zone of cyclohexanone distilled therefrom.

Although the preparation of hydroxylamine from nitrate has been known for many decades and ways to improve known preparation methods have been investigated thoroughly over the years, presently known industrial processes, which are

generally of a continuous nature, still suffer from drawbacks, especially when trying to increase the production capacity in an existing plant, or in a new plant based on a known design.

A way to increase the productivity in the reactor (at fixed concentration of hydroxylamine) is, for instance, reducing the liquid residence time, in combination with an increased catalyst concentration and/or an increased temperature and/or an increased hydrogen partial pressure. At some point it is not possible anymore to further increase the liquid feed rate without need for high investments in other parts of the loop.

A way to further increase the productivity is by increasing hydroxylamine concentration as is for instance described in EP-1,303,480-B1 and US-6,759,556. By increasing the hydroxylamine concentration a more efficient hydroxylamine conversion is obtained in its reaction with cyclohexanone in the downstream oximation reaction step. By also increasing the phosphate concentration (at a phosphate/hydroxylamine ratio > 2 mol/mol) less carbonyls (which act as a poison for the catalyst) enter the inorganic process loop, which is advantageous for high activity and selectivity of the hydrogenation catalyst.

The inventors realized that increasing hydroxylamine concentration is however problematic. For instance, during proprietary investigations in a conventional plant, the present inventors found that increasing the feed rate of reagents, in order to increase hydroxylamine production capacity, may give rise to fouling problems, in particular due to crystallization of, in particular, (mono)ammonium hydrogen phosphate salt(s). The fouling may result in clogging of, *e.g.*, filters or cooling pipes, downstream of the reaction zone. In particular, the inventors found that by raising the hydroxylamine product concentration and at the same time keeping the process conditions on advantageous values for the processes described in EP-1,303,480-B1 and US-6,759,556 the crystallization temperatures in the process liquid present in the inorganic process loop is increased.

Should the temperature of reaction mixture drop below its crystallization temperature, crystals will form. If this occurs on the surface of the reactor where cooling occurs, the crystal will insulate the reaction from cooling, and a loss of process control will occur. This could easily accelerate to severe fouling and a need to stop the reactor for cleaning; a severe disruption. To avoid fouling and process disorder the crystallization temperature of the reaction mixture should ideally remain higher than the temperature of the cooling water used to remove the heat of the hydrogenation

reaction. This limits the maximum hydroxylamine product concentration at which the nitrate hydrogenation reactor can be operated.

It is an object of the present invention to provide a novel method for preparing hydroxylamine in a continuous process that may serve as an alternative to known methods, in particular a novel method that can be operated at an increased hydroxylamine production capacity, compared to a conventional method operated in the same production facility, whilst crystallization of salts, like ammonium hydrogen phosphate salts is avoided.

It is a further object to provide a method for preparing hydroxylamine that requires less catalyst per ton of hydroxylamine prepared.

One or more further objects that may be addressed by the present invention will be apparent from the description herein below.

It has now surprisingly been found that one or more of these objects are addressed by performing the preparation of hydroxylamine at a nitrate concentration, and at a nitrate to phosphate ratio, and at an ammonia to nitrate ratio in the reaction zone, wherein hydroxylamine is formed, in a specific range.

Accordingly, the present invention relates to a method for preparing hydroxylamine in a continuous process, comprising feeding nitrate and phosphate in an acidic aqueous liquid into a reaction zone and reducing nitrate with hydrogen thereby forming hydroxylamine, wherein the feed of nitrate and phosphate, the hydrogen and the temperature are controlled such that the nitrate concentration in the reaction zone is less than 1.0 mol/kg, as determined in liquid leaving the reaction zone; the molar ratio of nitrate to phosphate in the reaction zone is 0.5 or less; and the molar ratio of ammonia to nitrate is in the range of from 2.2 to 7. The reduction of nitrate is generally a catalysed reaction.

It has been found that in accordance with the invention the preparation process of hydroxylamine can be intensified, whereby the production capacity is increased. It is surprising that at the relatively low nitrate concentration and relatively low nitrate to phosphate ratio an improved production capacity is feasible. After all, the nitrate hydrogenation reaction is thought to follow a Langmuir-Hinshelwood kinetics kind of behaviour, wherein the reaction rate is known to increase with increase of the concentration of nitrate in the reaction zone. Thus, it would be expected by a person of ordinary skill in the art that the nitrate reduction rate - and thereby the hydroxylamine production capacity - would be reduced by reduction of the nitrate concentration.

The specific parameters of nitrate concentration in the reaction zone of less than 1.0 mol/kg, as determined in the liquid leaving the reaction zone; molar ratio of nitrate to phosphate in the reaction zone of 0.5 or less; and molar ratio of ammonia to nitrate in the range of from 2.2 to 7, lead to reaction mixtures having particularly low crystallization temperatures, but which retain high conversion to hydroxylamine.

Thus, the present invention surprisingly provides a way to prepare hydroxylamine at an advantageous production capacity, with a reduced risk of fouling due to crystallization of substances in the reaction zone.

It is in particular contemplated that in accordance with the invention it is possible to obtain hydroxylamine in a reaction liquid (leaving the reaction zone) in a concentration of 1.2 mol/kg or more; preferably 1.3 or more, more preferably 1.4 or more, or 1.5 or more. Such a high hydroxylamine concentration is advantageous because the reaction system is thus intensified and productivity is improved. In a preferred embodiment the hydroxylamine concentration is 2 mol/kg or less, in particular 1.9 mol/kg or less, more in particular 1.8 mol/kg liquid reaction product or less. However, it is not prima facie obvious to operate at increased hydroxylamine concentration in the nitrate reduction reactor in view of the risks of crystallization and fouling that would be expected.

Further, a method according to the invention is advantageous in that less catalyst may be needed per produced quantity of hydroxylamine in order to realise a specific production capacity.

It has further been found that a method according to the invention is advantageous with respect to the further use of hydroxylamine in the preparation of an oxime, such as cyclohexanone oxime. The hydroxylamine usually leaves the reaction zone in a product reaction mixture, which typically is an aqueous liquid comprising the hydroxylamine, phosphate, any unreacted nitrate, and ammonia. The reaction product mixture from the hydroxylamine preparation is found to be particularly suitable as a feed for a method for preparing an oxime, the advantage residing in a more effective oximation reaction and/or oxime extraction from the oximation reaction product mixture,.

The term “or” as used herein means “and/or” unless specified other wise.

The term “a” or “an” as used herein means “at least one” unless specified other wise.

When referring to a 'noun' (*e.g.* a compound, an additive *etc.*) in singular, the plural is meant to be included, unless specified otherwise.

The preparation of hydroxylamine can suitably be carried out in a known continuous reactor for preparing hydroxylamine. In an embodiment, the reaction is carried out in a reactor providing well mixed gas/liquid systems. Such systems are well-known in the art and include stirred tank reactors, internal loop reactors, external loop reactors, and bubble column reactors. In a preferred embodiment, a bubble column reactor is used. Good results have in particular been achieved using a bubble column reactor with external gas-lift.

The concentration of the substance or a concentration derived parameter (such as a ratio of concentrations of substances) in the reaction zone can be determined by determining that parameter in a sample taken from the process liquid leaving the reaction zone.

As indicated above, in accordance with the invention the nitrate concentration in the reaction zone is less than 1.0 mol/kg, as determined in the liquid leaving the reaction zone. In a preferred embodiment, the nitrate concentration is 0.9 mol/kg or less, in particular 0.8 mol/kg or less. Particularly good results have been achieved with a nitrate concentration of about 0.70 or less. Usually, the nitrate concentration is at least 0.3 mol/kg, in particular at least 0.4 mol/kg. Preferably, the nitrate concentration is at least 0.45 mol/kg, more preferably at least 0.50 mol/kg.

The molar ratio of ammonia to nitrate is in the range of from 2.2 to 7. A molar ratio of 6 or less, in particular of 5 or less, is particularly preferred for a high productivity. It is in particular contemplated that this is advantageous for a high catalytic activity of the catalyst, with respect to catalysing the reduction of nitrate to form hydroxylamine. A molar ratio of ammonia to nitrate of 2.3 or more, in particular of 2.4 or more or of 2.5 or more is particularly preferred for a low fouling tendency. It is in particular contemplated that a molar ratio in the range of from 2.3 to 6, more preferably of from 2.4 to 5, or most preferably of from 2.5 to 5 is advantageous for a high catalytic activity of the catalyst, with respect to catalysing the reduction of nitrate to form hydroxylamine.

The phosphate is usually provided as phosphoric acid or a hydrogen phosphate salt (which may be formed by adjusting the pH of a phosphoric acid solution with an appropriate base, such as a hydroxide or ammonia). The molar ratio of nitrate to phosphate usually is at least 0.05, preferably at least 0.10. Excellent results are achieved at values of at least 0.15, more in particular of at least 0.20. The molar ratio of

nitrate to phosphate preferably is 0.40 or less, in particular 0.35 or less, more in particular 0.30 or less.

Hydrogen can be fed into the reaction zone in a manner and at a concentration (hydrogen pressure) known *per se*. Preferably, the pressure is at least approx. 0.5 MPa, more preferably at least approx. 1.0 MPa. Usually, the hydrogen pressure is 10 MPa or less.

In an advantageous embodiment, the buffer ratio is chosen within a specific range. Herein the buffer ratio is defined as:

$$([H^+] + [HYAM])/[phosphate]$$

wherein:

$[H^+]$ = molar concentration of H^+ in mol/kg in the aqueous liquid leaving the reaction zone.

[HYAM] = hydroxylamine concentration in mol/kg in the aqueous liquid leaving the reaction zone,

[phosphate] = total concentration of phosphate (including phosphate in H_3PO_4, monohydrogen phosphate and dihydrogen phosphate) in mol/kg, in the aqueous liquid leaving the reaction zone.

[H+], [HYAM] and [phosphate] concentrations are all determined by equilibrium titration of one sample, by subsequently titrating a sample of the liquid from the reaction zone at 25 °C with 0.25 N aqueous NaOH solution) to get the $[H^+]$ concentration ("free acid") at the first equilibrium point (at a pH of about 4.2); next molar excess of acetone is added to the sample, to convert hydroxylamine into an oxime and H^+, and equilibrium titration is continued so as to subsequently reach three further equivalence points, the first of which is corresponding to the free acid coming from hydroxylamine (and thus provides the value for [HYAM] in the sample); the second of which provides the value for [phosphate], and the last of which provides a value for ammonium. The latter value, however, is not needed here.

In particular for a low risk of crystallization taking place, also at a relatively high production capacity, the buffer ratio preferably is in the range of from 0.4 to 0.8, in particular in the range of from 0.45 to 0.70, more in particular in the range of from 0.50 to 0.65 mol/mol.

The molar H^+ concentration during the reaction is usually in the range of from 0.4 to 0.8 mol/kg, in particular in the range of from 0.45 to 0.70 mol/kg, more in

particular in the range of from 0.50 to 0.65 mol/kg.

The preparation of hydroxylamine in accordance with the invention is in general catalysed by a metal catalyst. Suitable catalysts are generally known in the art. In particular, a catalyst comprising palladium may be used. The catalyst may comprise one or more (catalytic) metals, in particular palladium. The catalyst is usually provided on a carrier. In particular, good results have been achieved with a catalyst comprising palladium on carbon. Typically, the catalyst is provided with a promoter for the catalyst, such as germanium oxide. The promoter can be added at any time during the method of preparing hydroxylamine, as desired.

Further conditions at which the hydroxylamine is prepared may be as known in the art *per se*. The temperature may in particular be in the range of from 20 to 70 °C, preferably in the range of from 30 to 60 °C, in particular in the range of from 35 to 55 °C.

The hydroxylamine prepared in accordance with the invention may be recovered from the reaction product mixture obtained in the reaction zone by a conventional technique, or the reaction product mixture may be fed into a further process, such as into a method for preparing an oxime (optionally after it has been treated, *e.g.* to remove one or more undesired components).
Accordingly, the invention also relates to the use of hydroxylamine obtained in a method according to the invention for the preparation of an oxime.

The oxime may be prepared from the hydroxylamine in a manner know *per se.* The method typically comprises reacting hydroxylamine obtained in a method according to the invention with an alkanone. The alkanone may be cyclic or non-cyclic. Preferred cycloalkanones are cyclohexanone, to obtain cyclohexanone oxime, and cyclododecahexanone, to obtain cyclododecanone oxime. Butanone is a preferred non-cyclic alkanone; butanone oxime is then prepared.

In particular, the invention is further directed to a method for preparing cyclohexanone oxime, comprising hydroxylamine obtained in a method according to the invention with cyclohexanone. This method may be carried out in a manner known *per se*, *e.g.* as described in the above identified prior art, of which the contents are incorporated herein by reference with respect to suitable conditions.

A (cyclic) oxime obtained in accordance with the invention, may in particular be used for preparing a lactam. This can be accomplished by Beckmann rearrangement, in a manner known *per se.*

Thus cyclohexanone oxime obtained in accordance with the invention

may be used in the preparation of caprolactam. Accordingly, the invention is further directed to a method for preparing caprolactam, comprising subjecting cyclohexanone oxime, obtained in a method according to the invention to Beckmann rearrangement, thereby forming caprolactam. The preparation of caprolactam may be carried out in a manner known *per se*, *e.g.* as described in the above identified prior art, of which the contents are incorporated herein by reference with respect to suitable conditions.

Likewise, laurolactam is obtained in an embodiment of the invention by a method comprising subjecting cyclododecanone oxime, obtained in accordance with the invention, to Beckmann rearrangement, thereby forming laurolactam. This preparation step may also be carried out in a manner known *per se.*

The method for preparing a (cyclic) oxime, such as cyclohexanone oxime, and – if desired - the method for making a lactam there from, such as caprolactam, are usually integrated in a single plant wherein hydroxylamine, oxime and – if desired - lactam are prepared in a continuous process.

The method is now illustrated by the following examples.

Examples

Examples 1-5

The nitrate reduction was carried out in an industrial gas lift loop reactor consisting of a gassed riser section, a liquid-gas separation section, a gas recycle section, a filtration section to separate part of the circulating liquid as product (wherein concentrations shown in Table 1 were determined; these correspond to the concentrations in the reaction zone) from the catalyst-containing reactor liquid. Fresh hydrogen was fed to the reactor and a gas purge was applied such that the hydrogen partial pressure was maintained at approx. 1.4 MPa in the top section of the reactor. The average reactor temperature was maintained at approx. 50 ^{o}C. As catalyst 10 wt% Pd/C was used. As activator approx. 45 gram GeO_2 per kg Pd was added. The catalyst (as dry Pd/C) concentration based on the inorganic process liquid present in the reactor was approx. 1 wt%. Feeding rate and feed composition of the inorganic process liquid fed to the reactor were varied in wide ranges as shown in Table 1, resulting in different composition of the reactor product and hydroxylamine production rate. In Table 1 both data for the performance of the nitrate reduction reactor under reference conditions ('Plant ref.') and data for the performance of the nitrate reduction reactor in the process according to the invention in which nitrate concentration and nitrate to phosphate ratios have been reduced ('E1' up to and including 'E5'), in combination with increased values for ammonia versus nitrate ratios, are shown. The activity in Table 1 is based on the amount of catalyst (as dry Pd/C) present in the gassed riser zone of the hydrogenation reactor. The inorganic liquid product composition, as exemplified in Table 1 'E1' up to and including 'E5', may be compared with the composition of the inorganic liquid product as obtained in 7 experiments given in US-6,759,556 (for which crystallization temperatures were determined by the present inventors) and which are shown in Table 2.

Table 1: Plant experiments at reference conditions and at reduced nitrate and nitrate to phosphate ratios.

	NO_3^- [mol/kg]	PO_4 [mol	HYAM [mol/kg]	NH_4^+ [mol/kg]	H^+ [mol/kg]	Catalyst activity [mol HYAM/kg cat/hr]	Tcryst [°C]	NO_3/PO_4 [mol/mol]	NH_4^+/NO_3^- [mol/mol]	Buffer ratio [mol/mol]
Plant ref.	1.50	2.91	1.31	2.57	0.53	109	24	0.52	1.7	0.63
E1	0.26	3.61	1.66	1.68	0.53	163	19	0.07	6.5	0.61
E2	0.33	3.28	1.42	1.65	0.54	172	14	0.10	5.0	0.60
E3	0.54	3.56	1.51	2.03	0.56	184	23	0.15	3.8	0.58
E4	0.73	3.38	1.60	1.97	0.54	276	18	0.22	2.7	0.63
E5	0.97	3.15	1.34	2.18	0.60	216	19	0.31	2.3	0.61

PO_4 = total phosphate

Comparative Examples 1-7

Table 2: Liquid composition of the nitrate reduction reactor for high hydroxylamine concentrations according to US-6,759,556.

	NO_3^- [mol/kg]	PO_4 [mol/kg]	HYAM [mol/kg]	NH_4^+ [mol/kg]	H^+ [mol/kg]	Tcryst [°C]	NO_3^-/PO_4 [mol/mol]	NH_4^+/NO_3^- [mol/mol]	Buffer ratio [mol/mol]
Comp. Exp 1	1.47	2.58	1.10	2.64	0.31	26	0.57	1.8	0.55
Comp. Exp 2	1.38	2.69	1.04	2.48	0.55	20	0.51	1.8	0.59
Comp. Exp 3	1.32	2.67	1.20	2.48	0.31	24	0.49	1.9	0.57
Comp. Exp 4	1.34	2.88	1.22	2.52	0.49	24	0.46	1.9	0.59
Comp. Exp 5	1.32	3.10	1.20	2.48	0.74	21	0.43	1.9	0.63
Comp. Exp 6	1.37	2.79	1.33	2.58	0.25	28	0.49	1.9	0.57
Comp. Exp 7	1.32	3.14	1.28	2.48	0.70	22	0.42	1.9	0.63

PO_4 = total phosphate

Comparative Examples 8-10

Product mixtures were prepared to simulate the effect of product concentration on the resulting crystallization point of the product mixture. The composition of the product mixture was adjusted for key performance numbers like H^+ and buffer ratio at desired levels and NO_3^- concentration was at a level at which high reaction rates would be expected by a person of ordinary skill in the art. Table 3 shows in an otherwise conventional process window, but now at relatively high NO_3^- concentrations, relatively high NO_3^- to phosphate ratios and at relatively low NH_4^+ to NO_3^- ratios, that the crystallization temperatures of the product mixture increase at an increasing hydroxylamine product concentration, as compared to the results as shown in Table 1. It is to be noted that, for proper plant operation, crystallization temperatures preferably should be controlled below 25 °C and in particular below 20 °C. The results shown in Table 3 demonstrate that operating at high hydroxylamine concentrations generally leads to an increased risk of crystallization under conditions at a level at which high reaction rates would be expected by a person of ordinary skill in the art.

Table 3: Example of the effect of increased hydroxylamine product concentration on the crystallization temperature of the product mixture in the process window of NH_4^+/NO_3^- < 2.2 mol/mol

	NO_3^- [mol/kg]	PO_4 [mol/kg]	HYAM [mol/kg]	NH_4^+ [mol/kg]	H^+ [mol/kg]	Tcryst [°C]	NO_3^-/PO_4 [mol/mol]	NH_4^+/NO_3^- [mol/mol]	Buffer ratio [mol/mol]
Comp. Exp 8	1.33	3.14	1.41	2.53	0.53	26	0.42	1.9	0.62
Comp. Exp 9	1.34	3.31	1.53	2.57	0.55	28	0.40	1.9	0.63
Comp. Exp 10	1.35	3.57	1.67	2.71	0.54	34	0.38	2.0	0.62

PO_4 = total phosphate

CLAIMS

1. Method for preparing hydroxylamine in a continuous process, comprising feeding nitrate and phosphate in an acidic aqueous liquid into a reaction zone and reducing nitrate with hydrogen thereby forming hydroxylamine, wherein the feed of nitrate and phosphate, the hydrogen and the temperature are controlled such that the nitrate concentration in the reaction zone is less than 1.0 mol/kg, as determined in liquid leaving the reaction zone; the molar ratio of nitrate to phosphate in the reaction zone is 0.5 or less; and the molar ratio of ammonia to nitrate is in the range of from 2.2 to 7.

2. Method according to claim 1, wherein the molar ratio of ammonia to nitrate is in the range of from 2.3 to 6, in particular in the range of from 2.5 to 5.

3. Method according to claim 1 or 2, wherein the nitrate concentration is in the range of from 0.3 to 0.9 mol/kg, in particular in the range of from 0.4 to 0.8 mol/kg.

4. Method according to claim 1, 2 or 3, wherein the molar ratio of nitrate to phosphate is in the range of from 0.1 to 0.4, in particular in the range of from 0.10 to 0.30.

5. Method according to any of the preceding claims, wherein the buffer ratio in the reaction zone is in the range of from 0.4 to 0.8, in particular in the range of from 0.45 to 0.70, more in particular in the range of from 0.50 to 0.65.

6. Method according to any of the preceding claims, wherein the preparation of hydroxylamine is catalysed by a palladium-containing catalyst.

7. Method according to claim 6, wherein the catalyst is provided on a carbon carrier.

8. Method according to claim 6 or 7, wherein the catalyst further contains platinum.

9. Method according to any of the preceding claims, wherein the molar H^+ concentration is in the range of from 0.4 to 0.8 mol/kg, in particular in the range of from 0.45 to 0.70 mol/kg, more in particular in the range of from 0.50 to 0.65 mol/kg.

10. Method according to any of the preceding claims, wherein the temperature in the reaction zone is in the range of from 20 to 70 °C, preferably in the range of from 30 to 60 °C, in particular in the range of from 35 to 55 °C.

11. Method for preparing an oxime, comprising a method as defined in any of the

preceding claims followed by reacting the hydroxylamine with an alkanone, in particular an alkanone selected from the group of cyclohexanone, cyclododecahexanone and butanone.

12. Method according to claim 11, wherein the alkanone is cyclohexanone and the oxime is cyclohexanone oxime.

13. Method for preparing caprolactam, comprising a method as defined in claim 12 followed by subjecting the cyclohexanone oxime to Beckmann rearrangement.

14. Method according to claim 11, wherein the alkanone is cyclododecahexanone and the oxime is cyclododecanone oxime.

15. Method for preparing laurolactam, comprising a method as defined in claim 14 followed by subjecting the cyclododecanone oxime to Beckmann rearrangement.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/056923

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B21/14
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)
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	EP 1 947 056 A1 (CHINA PETROCHEMICAL DEV CORP [TW]) 23 July 2008 (2008-07-23) cited in the application examples paragraphs [0018] - [0026]	1-15
X	US 2006/079678 A1 (OEVERING HENDRIK [NL] ET AL) 13 April 2006 (2006-04-13) cited in the application paragraphs [0001] - [0003], [0011], [0026] - [0033]	1-15
A	EP 1 329 448 A1 (UBE INDUSTRIES [JP]) 23 July 2003 (2003-07-23) cited in the application paragraphs [0001] - [0003]	1-15

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
4 June 2012	13/06/2012

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/056923

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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