

Preparation of hydroxylammonium salts

- 5 The present invention relates to a process for preparing hydroxylammonium salts by catalytic reduction of nitrogen monoxide with hydrogen in the presence of an acid and a hydrogenation catalyst.
- 10 Hydroxylamine is widely used for, in particular, the preparation of caprolactam. It is nowadays prepared on an industrial scale by, inter alia, reduction of nitrogen monoxide with hydrogen. The nitrogen monoxide is in turn obtained by reacting ammonia and oxygen by the Ostwald process and is used directly in the
- 15 hydroxylamine synthesis. Here, the nitrogen monoxide is purified in a scrubber and converted into hydroxylamine by reaction with hydrogen below 50°C using a suitable supported noble metal catalyst in sulfuric acid suspension. This produces small amounts of ammonium sulfate and dinitrogen monoxide as by-products. In
- 20 general, use is made of supported platinum catalysts whose selectivity to hydroxylamine is maximized by partial poisoning.

DE-A-956 038 describes a process for preparing hydroxylammonium salts in which the reduction of nitrogen monoxide is carried out

25 over platinum/graphite catalysts which are obtained by reductive precipitation of platinum onto suspended graphite supports, if appropriate with addition of catalyst poisons such as sulfur, selenium, arsenic or tellurium compounds. These catalysts have the disadvantage that the reactivity and selectivity decreases

30 quickly on prolonged use.

DE-A-40 22 851 describes platinum/graphite catalysts for the hydrogenation of nitrogen monoxide whose selectivity is related to the apparent density, compressive strength and porosity of the

35 graphite support.

DE-A-40 22 853 describes platinum/graphite catalysts in which the graphite support has a certain particle size distribution in the range from 1 to 600 μm . When using these catalysts, the

40 selectivity of hydroxylamine formation in the hydrogenation of nitrogen monoxide can be increased.

In the known methods of preparing hydroxylamine, the selectivity of the nitrogen monoxide formation, the space-time yields and the

45 operating lives of the catalysts are capable of improvement.

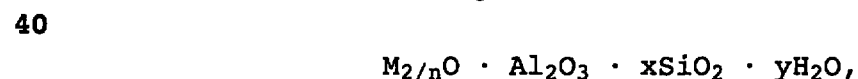
The nitrogen monoxide prepared by combustion of ammonia contains other NO_x compounds such as NO_2 and N_2O as well as numerous further impurities in the ppm range of which the most important are H_2S , CO_2 , CO , CH_4 and other hydrocarbons. DE-A-15 42 628 has already described a process for selectively removing nitrogen dioxide and/or molecular oxygen by catalytic reduction with reducing gases using catalysts which comprise silver and possibly manganese in the form of their oxidic compounds as active components. However, this process is too complicated for industrial use because it requires an additional hydrogenation step and an additional catalyst. In addition, the removal of NO_2 is insufficient and the concentration of dinitrogen monoxide is increased.

It is an object of the present invention to provide an improved process for preparing hydroxylammonium salts by reduction of NO with hydrogen which is technically simple to carry out and gives high selectivities and space-time yields. In addition, the catalyst should have a relatively long operating life.

We have found that this object is achieved by purifying the nitrogen monoxide in a simple manner by treatment with porous oxides based on silicon or aluminum or with activated carbon, since we have discovered that the purity of the nitrogen monoxide used influences the abovementioned parameters.

The present invention accordingly provides a process for preparing hydroxylammonium salts by catalytic reduction of nitrogen monoxide with hydrogen in the presence of an acid and a hydrogenation catalyst, wherein the nitrogen monoxide is purified before the catalytic reduction by subjecting it to at least one treatment with porous oxides based on silicon and/or aluminum or with activated carbon.

Porous oxides which can be used are, in particular, silicon dioxides such as silica gel and molecular sieves. Molecular sieves are, as is known, natural or synthetic zeolites, i.e. aluminum silicates containing alkali metal or alkaline earth metal cations and having the formula



where M is an alkali metal or alkaline earth metal, n is the valence of the cation and $x \geq 2$. The pore diameter of the molecular sieves is frequently given in Å, i.e. a molecular sieve designated as 3 Å has a pore opening of 3 Å (0.3 nm).

According to the present invention, preference is given to molecular sieves 5A and in particular molecular sieves 4A.

The oxides, in particular the molecular sieves, are frequently employed in a state containing a little water or an essentially anhydrous state.

Activated carbons which can be used are commercial activated carbons such as Degusorb, Contarbon BA, Supersorbon K or Desorex A.

According to the present invention, it has been found to be particularly advantageous to dry the nitrogen monoxide before the purification. Customary materials can be used for this purpose, but it has been found to be particularly useful to employ one of the abovementioned porous oxides, in particular silica gel, for the drying step. In a particularly preferred embodiment, the nitrogen monoxide is therefore treated first with silica gel for the purpose of drying (and initial purification) and then with a molecular sieve for further purification.

Both drying and purification can be carried out in one or more stages and using one or more desiccants or purification agents. In general, drying and purification are carried out in customary apparatuses, but it has been found to be advantageous to carry out drying and purification in appropriately dimensioned towers.

For purifying about 10 standard l/h of NO, use is usually made of from 1000 to 1500 ml of the purification agent and about the same amount of desiccant. The purification towers are generally regenerated by baking out after from about 8 to 12 operating hours. The drying towers are baked out after from about 300 to 400 operating hours.

Both the temperature and the pressure employed in purification and drying of the nitrogen monoxide can be varied within a wide range. In general, drying and/or purification are carried out at from 20 to 500°C, in particular from 20 to 150°C, and at a pressure in the range from 100 mbar to 100 bar, in particular from 800 mbar to 2 bar, but most expediently at about atmospheric pressure.

Analysis of nitrogen monoxide before and after purification shows that, in particular, the content of other nitrogen oxides such as N₂O and NO₂, which occur in the percentage range, and the content

of H_2S , which occurs in the ppm range, are decreased greatly. This can be seen from Table 3 in Example 3.

The hydrogenation which follows the purification step is carried out in a manner known per se. Preferably, hydrogen and nitrogen monoxide are reacted in a molar ratio in the range from 1.5:1 to 6:1. Particularly good results are obtained when a molar ratio of hydrogen to nitrogen monoxide of from 3.5:1 to 5:1 is maintained in the reaction zone.

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Hydrogenation catalysts employed are those which are customarily used for this purpose. Preference is given to using platinum-on-graphite catalysts as are described in DE-A-40 22 853. In particular, the catalyst is treated in acid solution before hydrogenation, advantageously in the acid in which the hydrogenation is carried out. This leads to activation of the catalyst.

The hydrogenation is carried out in the presence of an acid, preferably a strong mineral acid such as nitric acid, sulfuric acid or phosphoric acid, or an aliphatic C_1 - C_5 -monocarboxylic acid such as formic, acetic, propionic, butyric or valeric acid, preferably formic or acetic acid. Acid salts such as ammonium bisulfate are also suitable. In general, from 4 to 6 N aqueous acids are used and care is taken to ensure that the acid concentration does not drop below 0.2 N during the course of the hydrogenation. If necessary, further acid is added.

The ratio of acid to catalyst depends significantly on the catalyst used. In general, it is in the range from 1 to 150 g of catalyst per liter of mineral acid. In the case of the abovementioned platinum catalyst described in DE-A-40 22 853, the ratio is preferably in a range from 1 to 100 g, in particular from 20 to 80 g, of catalyst per liter of mineral acid.

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The hydrogenation is generally carried out at from 30 to 80°C, preferably from 35 to 60°C. The pressure during the hydrogenation is usually selected in the range from 1 to 30 bar, preferably from 1 to 20 bar (absolute).

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The process of the present invention for preparing hydroxylammonium salts gives significantly higher hydroxylammonium selectivities and lower dinitrogen monoxide selectivity. In addition, the space-time yield of catalysts which are exposed to purified nitrogen monoxide in accordance with the process of the present invention is considerably increased compared to the use of untreated nitrogen monoxide. Furthermore,

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the operating life of the catalysts used is also increased. As a result, the catalyst has to be regenerated less often, which improves the economics of the process.

- 5 The following examples illustrate the invention without restricting it.

Example 1

- 10 a) 40 g of a graphite from Asbury having a particle size of from 2 to 50 μm and 0.5310 g of hexachloroplatinic(IV) acid hexahydrate were stirred overnight at 80°C in an aqueous solution comprising 3.87 ml of concentrated hydrochloric acid and 0.87 ml of concentrated nitric acid. Sodium carbonate was
15 added to the suspension obtained until the pH was 2.75. Subsequently, 2.5 g of sodium acetate were added as a buffer. 5 mg of elemental sulfur were then added and, after waiting for 2 minutes, the resulting suspension was admixed with 14.1 g of a 40% strength by weight aqueous sodium formate
20 solution (83 mmol) and stirred at 80°C for 4 hours. After this time, platinum could no longer be detected by means of hydrazine hydrate (gives a black precipitate in alkaline solution in the presence of platinum).
- 25 The catalyst prepared in this way was separated from the reaction mixture by filtration through a glass frit and washed with distilled water until the pH of the washings was no longer in the acid range. The dried catalyst contained 0.5% by weight of platinum.
- 30 b) 3.6 g of the catalyst prepared under a) were suspended in 120 ml of 4.3 N sulfuric acid and, at 40°C while stirring vigorously (3500 rpm), 7.75 l/h of a mixture of 35% by volume of nitrogen monoxide which had previously been passed through
35 a drying tower filled with 800 ml of silica gel and subsequently through a purification tower filled with 1200 ml of molecular sieves 4A (Carl Roth GmbH, Karlsruhe) and 65% by volume of hydrogen were passed into the suspension. After 4 hours, the catalyst was separated off and the liquid phase
40 was analyzed. The catalyst which had been separated off was subsequently mixed with 120 ml of 4.3 N sulfuric acid and the reaction was continued. This procedure was repeated every four hours and will be designated as a batch. The catalyst was tested until the hydroxylamine synthesis changed by less
45 than 0.5% from batch to batch (activation phase). This required a catalyst running time of 20 batches. In the 21st batch, unpurified NO was then used; in the 22nd batch,

purified NO as in the previous batches was again used. The liquid phase was analyzed in each case. The selectivities achieved in these batches are shown in Table 1.

5 Table 1

	Batch	20	21	22
	NO purification	Molecular sieve 4A	-	Molecular sieve 4A
10	Selectivity to NH_2OH [%]	90.93	87.17	90.76
	Selectivity to NH_3 [%]	8.47	8.40	8.92
	Selectivity to N_2O [%]	0.60	4.42	0.32
	NO conversion [%]	95.16	94.75	94.79
15	Space-time yield	0.872	0.833	0.867

It can be seen from Table 1 that the use of unpurified NO leads to a substantial increase in the NO_2 selectivity, mainly at the expense of the hydroxylamine selectivity. If purified NO is again used in the following batch, the values of the batch before are achieved again.

Example 2

25 Passing the NO through a drying tower

3.6 g of the catalyst prepared in Example 1a) were suspended in 120 ml of 4.3 N sulfuric acid and, at 40°C while stirring vigorously (3500 rpm), 7.75 l/h of a mixture of 35% by volume of nitrogen monoxide which had previously been passed through a drying tower filled with 800 ml of silica gel and 65% by volume of hydrogen were passed into the suspension. After 4 hours, the catalyst was separated off and the liquid phase was analyzed. The catalyst which had been separated off was subsequently mixed with 120 ml of 4.3 N sulfuric acid and the reaction was continued. This procedure was repeated every four hours. The reaction was stopped when the selectivity to dinitrogen monoxide exceeded the predetermined upper limit of 5%. The experimental results are shown in Table 2.

40 Example 3

Passing the NO through a drying tower and a purification tower

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3.6 g of the catalyst prepared in Example 1a) were suspended in 120 ml of 4.3 N sulfuric acid and, at 40°C while stirring vigorously (3500 rpm), 7.75 l/h of a mixture of 35% by volume of nitrogen monoxide which had previously been passed through a drying tower filled with 800 ml of silica gel and subsequently through a purification tower filled with 1200 ml of molecular sieves 4 A (Carl Roth GmbH, Karlsruhe) and 65% by volume of hydrogen were passed into the suspension. After 4 hours, the catalyst was separated off and the liquid phase was analyzed. The catalyst which had been separated off was subsequently mixed with 120 ml of 4.3 N sulfuric acid and the reaction was continued. This procedure was repeated every four hours. The reaction was stopped after 50 batches. The selectivity to dinitrogen monoxide was 0.41% at this point. The results achieved are shown in Table 2.

Table 2

	Example 2	Example 3
NO purification	Drying tower	Drying tower, purification tower
Selectivity to NH_2OH [%]	89.70	90.05
Selectivity to NH_3 [%]	7.87	9.27
Selectivity to N_2O [%]	2.43	0.68
NO conversion [%]	97.34	95.88
Space-time yield	0.880	0.871
Operating life [batches]	30	>54

It can be seen from the table that the catalyst exposed to NO which has previously been passed only through a drying tower has a shorter operation life at comparable hydroxylamine selectivities and space-time yields. It is therefore clear that molecular sieves free the NO of additional impurities which lead to accelerated aging of the catalyst. To clearly show the purification effect, the content of impurities in unpurified NO and in NO purified in different ways (drying tower containing silica gel or molecular sieves 4A) is shown in Table 3.

Table 3

	NO	N ₂ [%]	O ₂ [ppm]	CO [ppm]	CO ₂ [ppm]	CH ₄ [ppm]	C ₂ H ₄ [ppm]	N ₂ O [%]	NO ₂ [%]	H ₂ S [ppm]
5	Steel bottle	0.82	1.0	<1	<5	<2	1	0.6677	0.7942	4.1
	through drying tower	0.57	1.2	<1	<5	<2	1	0.6883	0.0090	1.1
10	over mole- cular sieves 4A	0.62	1.2	<1	<5	<2	<1	0.2574	0.0044	0.4

15 The values were obtained by separation of the NO to be analyzed in columns of the type indicated below or using the methods indicated.

Molecular sieve 5A; 50 m; 0.32 mm; (inert gases)

20 Activated carbon; 2 m; 4 mm; (hydrogen)
 Poraplot Q; 50 m; 0.53 mm; (carbon dioxide)
 Al₂O₃/KCl; 100 m; 0.53 mm; (hydrocarbons)
 GC atomic emission technique (H₂S)
 IR spectroscopy (N₂O, NO₂)

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We claim:

1. A process for preparing hydroxylammonium salts by catalytic
5 reduction of nitrogen monoxide with hydrogen in the presence
of an acid and a hydrogenation catalyst, wherein the nitrogen
monoxide is purified before the catalytic reduction by
subjecting it to at least one treatment with porous oxides
based on silicon and/or aluminum or with activated carbon.
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2. A process as claimed in claim 1, wherein the porous oxide
used is a molecular sieve or a silica gel.
3. A process as claimed in claim 1 or 2, wherein the nitrogen
15 monoxide is subjected to a drying step before purification.
4. A process as claimed in claim 2 or 3, wherein the nitrogen
monoxide is first passed over silica gel and subsequently
over a molecular sieve, in particular a molecular sieve
20 having the pore size 4A.
5. A process as claimed in any of the preceding claims, wherein
the purification is carried out at from 20 to 500°C, in
particular from 20 to 150°C.
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6. A process as claimed in any of the preceding claims, wherein
the purification is carried out at a pressure in the range
from 100 mbar to 100 bar, in particular from 800 mbar to
2 bar.
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7. A process as claimed in any of the preceding claims, wherein
the catalytic reduction is carried out at from 30 to 80°C and
at a pressure in the range from 1 to 30 bar.
- 35 8. A process as claimed in any of the preceding claims, wherein
the hydrogenation is carried out using a molar ratio of
hydrogen to nitrogen monoxide in the range from 3.5:1 to 5:1.
9. A process as claimed in any of the preceding claims, wherein
40 the acid used is sulfuric acid, nitric acid or phosphoric
acid.