

The invention relates to a process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, using the silver-containing supported catalyst.

5 The catalytic decomposition of nitrous oxide (laughing gas) has been known for a long time and is described in numerous publications in the context of kinetic studies. As early as 1936, in Gmelins Handbuch
10 der anorganischen Chemie, Stickstoff, 8th Edition, page 573 ff, the decomposition of nitrous oxide in a quartz vessel in the presence or absence of various catalysts such as SiO_2 , platinum foil, titanium dioxide, platinum
15 black, Al_2O_3 , wood charcoal or thorium dioxide was studied at various temperatures. Kinetic studies over pure silver, over silver-gold and silver-calcium alloys are described by K.E. Hayes, Canad. J. Chem. 37, (1959) 583. In Catalysis Today 4, (1989) 235 - 251, R. Larsson gives
20 an overview of the activation energies for nitrous oxide decomposition over oxidic catalysts, particularly over mixed oxides.

 Industrial interest in the decomposition of nitrous oxide to give nitrogen and oxygen was generated by NASA which, starting from ammonium nitrate via laughing
25 gas, wanted to utilize the decomposition into the elements to produce breathing air for astronauts from a compound which is easy to handle (Chem. Abstract 6 1481 (1965)). Catalysts which were described as suitable are: platinum on various inorganic supports, rhodium on
30 aluminum oxide and nickel, cobalt and molybdenum oxides.

 A further industrial field of application is the elimination of anesthesia gases, for example in operating
35 theaters. There is a series of Japanese patents pertaining to this application. The following catalyst systems are mentioned: activated carbon (in JP 54/11090), elements of the iron group in combination with rare earth metals (JP 61/45487), platinum, palladium, rhodium, indium and/or ruthenium (JP 55/31463) and copper oxide, chromium oxide on aluminum oxide (JP 61/50650). Nitrous oxide is generally decomposed in a nitrous oxide/air

mixture (1:1). JP 61/53142 describes the removal of nitrous oxide from waste gases over cobalt, copper and manganese oxides on gamma-aluminum oxide.

DE-A 3 543 640 discloses palladium-containing catalysts for the decomposition of nitrous oxide.

JP 63/07826 describes the removal of nitrous oxide from waste gases, inter alia over palladium or copper oxide on gamma-aluminum supports. In the example, the N_2O concentration in the gas is 26 ppm.

Finally, SU 1 011 238 describes the decomposition of nitrous oxide over carbides on $CaCl_2$ as support.

In all the abovementioned publications, nitrous oxide/air or nitrous oxide/oxygen mixtures are reacted. According to DE-A 3 543 640, mixtures containing 430 ppm of NO_x and 4% of water (gaseous) are also reacted over palladium catalysts.

German Application 40 29 061.1, which is not a prior publication, describes silver-containing supported catalysts on Al_2O_3 , with the Al_2O_3 having a BET surface area of from 5 to 25 m^2/g .

It is an object of the present invention to provide a process for the catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, by means of which nitrous oxide can, even in the presence of relatively high concentrations of nitrogen oxides and other gases which are not oxygen or nitrogen, in particular waste gases which are formed in the preparation of adipic acid, for example by oxidation of cyclohexanol and cyclohexanone using nitric acid) be decomposed into the elements nitrogen and oxygen. A further problem to be solved here is the selective degradation of nitrous oxide without other nitrogen oxides being decomposed into the elements.

We have found that this object is achieved by means of silver-containing supported catalysts comprising from 0.1 to 40% by weight of silver, based on the total catalyst, and an aluminum oxide support having mesopores and macropores and a BET surface area of from 26 to 350 m^2/g .

The present invention provides a process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, at from 200 to 1000°C over silver-containing supported catalysts, wherein the supported catalyst comprises from 0.1 to 40 % by weight of silver, based on the total catalyst, and an aluminum oxide support having mesopores and macropores and a BET surface area of from 26 to 350 m²/g.

The advantage of this process is that nitrous oxide, either in very pure form, in mixtures with oxygen or air or in mixtures with air containing relatively large amounts of water and/or relatively large amounts of nitrogen oxides (nitrogen monoxide, nitrogen dioxide), can be selectively decomposed into the elements nitrogen and oxygen without the higher nitrogen oxides being degraded in the process. Nitrous oxide in mixtures containing, for example, up to 50% of nitrogen dioxide (NO₂) and/or 20% of water can easily be decomposed into its elements.

Suitable methods for producing the supported catalysts are in principle all methods which have been proposed in the literature for producing silver-containing supported catalysts (cf., for example D.I. Hucknall, Selective Oxidations of Hydrocarbons, Academic Press, London (1974), page 6). For example, a suspension of freshly precipitated, well washed silver oxide (DE-B 12 11 607) or silver carbonate (US-A 3 043 854) can be rolled onto a support and the silver compound can be subsequently thermally decomposed into silver. A preferred method is impregnating a coarse-porosity support with the solution of a silver salt, such as silver nitrate (US-A 3 575 888) or silver lactate (DE-B 12 11 607) or a silver complex (eg. a silver-amine-carboxylate complex (DE-A 21 59 346)) and subsequently decomposing the silver compound into elemental silver by treatment with a reducing agent or by heat treatment.

For the production of the supported catalysts using silver-amine complexes, reference is made, in particular, to German Application 4 029 061.1, where this

process is described in more detail.

The catalysts used in the process of the present invention contain from 0.1 to 40% by weight, in particular from 2 to 25% by weight, of silver based on the weight of the total catalyst. The silver particle size in the unused catalyst is from 0.1 to 200 nm, preferably from 1 to 100 nm, in particular from 2 to 50 nm. The silver particle size can be determined, for example, by XRD (X-ray diffraction).

The aluminum oxide supports used for the process of the present invention have a BET surface area of from 26 to 350 m²/g. (For the preparation of such aluminum oxides see, for example, Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A1, p. 588-590; VCH, 1985). The BET surface area is preferably from 40 to 300 m²/g, in particular from 50 to 250 m²/g. The BET surface areas were measured using a commercially available single-point BET instrument ("Areamat 1" from Ströhlein). In the region of these surfaces, aluminum oxide can be present in the alpha, kappa, beta, delta, theta or gamma phase. In addition, the simultaneous presence of two or more phases is possible. The support used can consist of pure aluminum oxide or of mixtures with other oxides. The doping of high surface area aluminum oxide supports, ie. the formation of mixed oxides, leads to an increase in the thermal resistance of the support (eg. DE 3 403 328, DT 2 500 548, Appl. Catal. 7, (1983) 211-220, J. Catal. 127, (1991) 595-604). In addition, the foreign ions can contribute to the catalytic activity of the catalyst. Doping can be carried out using, in general, the following elements: alkali metals, alkaline earth metals, metals of the rare earths, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, B, Si, Ge, Sn, Pb, P, Bi. The degree of substitution of aluminum oxide can be, for example, from 0.01 to 50% by weight. Calcination of the doped support can lead to formation of a spinel phase.

The porosity of the support is such that mesopores and macropores are present in the aluminum oxide

support. The proportion of pores having a diameter of from 1 to 100 nm is here preferably from 20 to 80%, in particular from 30 to 70%. In addition, there should be further pores in the range from 0.1 to 10 μm and in the range from 10 to 1000 μm . The proportion of pores having a diameter of from 0.1 to 10 μm should be in the range from 0 to 60% and that of those having a diameter from 10 to 1000 μm should be in the range from 0 to 30%, with pores from at least one of these two pore diameter ranges being present in addition to the pores having a diameter of from 1 to 100 nm. The distribution of the pores in the two ranges 0.1 - 10 μm and 10 - 1000 μm should be such that it is narrow in the range of the smaller pores and broader in the range of the larger ones. In general, the proportion of pores in the range from 0.1 to 10 μm is higher than that in the range from 10 to 1000 μm . Alternatively, one of the two last-named pore groups can be missing without the activity of the catalyst being reduced thereby. For this reason, both bimodal and trimodal pore distributions can result. The pore volume of the support (determined by H_2O absorption) is preferably from 35 to 80 ml/g, which corresponds approximately to a value of from 30 to 75 ml/g measured by Hg porosimetry. Suitable supports are commercially available.

In addition to silver, other active components (promoters), in particular Cu, Au, Pd, Pt, can be present in the catalyst in amounts of up to 40% by weight, preferably up to 20% by weight, based on the total amount of the active component. The supported catalysts of the present invention can be in the form of pellets, honeycombs, rings, chippings, solid and hollow extrudates or other geometric shapes ("shaped catalysts", see, for example, US 2 408 164, GB 2 193 907, US 4 233 187).

For certain applications it is important that shape and size be selected so that a very small pressure drop results.

In the process of the present invention, nitrous oxide or a nitrous oxide-containing gas mixture is passed at from 200 to 1000°C over the supported catalyst and is

thus decomposed into nitrogen and oxygen. The temperatures are preferably from 300 to 900°C, in particular from 400 to 850°C. The temperatures at the reactor inlet are from 200 to 700°C, while in the catalyst bed the temperature can increase as a result of the exothermic decomposition of the N_2O . The GHSV (Gas Hourly Space Velocity) can be from 500 to 10,000 standard l of gas/l of cat•h, preferably from 1500 to 6000 standard l of gas/l of cat•h.

The process of the present invention is generally carried out by preheating pure nitrous oxide or nitrous oxide-containing gas mixtures or nitrous oxide-containing waste gas to the necessary reactor temperature, eg. in a furnace or heat exchanger, and then passing it through a reaction tube packed with the silver catalyst. The preheating of the reaction gas can also be carried out directly in the reaction tube by means of an upstream inert material bed.

In addition to the N_2O , the gas mixture being treated by the process of the present invention can also contain, in particular, NO and/or NO_2 in an amount of from 0.01 to 50% by volume, based on the total gas. The N_2O content of the gas mixture is preferably from 0.01 to 50% by volume, in particular from 0.1 to 30% by volume. Apart from N_2O and NO/ NO_2 (NO_x), the gas mixture can also contain N_2 , O_2 , CO, CO_2 , H_2O and noble gases.

The pressure range in which the process is generally carried out is from 0.1 to 20 bar, ie. sub-atmospheric or superatmospheric pressure can be used. Preference is given to carrying out the process at atmospheric pressure.

The catalyst of the present invention and the process of the present invention are particularly suitable for decomposing N_2O in the waste gases which are formed in the preparation of adipic acid, for example in the oxidation of cyclohexanol and/or cyclohexanone using nitric acid.

A particular advantage of the process is that N_2O is selectively decomposed, ie. decomposition of NO_x as

desired product does not take place.

The process of the present invention makes it possible to carry out the catalytic decomposition of nitrous oxide either in pure form or in gas mixtures. The invention represents a significant improvement both from an economic point of view and in respect of the performance of the catalyst.

Examples

Decomposition of nitrous oxide:

The test apparatus comprised an 80 cm long reaction tube of Hasteloy C, divided into heating and reaction zones. The internal diameter is 18 mm. So as to be able to measure the temperature profile in the tube, an inner tube having an external diameter of 3.17 mm, in which a thermocouple can easily be moved, was inserted. To improve the heat transfer, the reactor was packed with inert material (steatite) in the heating zone. Tests were carried out on 40 ml of each catalyst (chippings 1.5 - 2 mm) at atmospheric pressure.

Typical gas composition:

N ₂ O:	23 % by volume;
NO+NO ₂ :	17 % by volume;
N ₂ :	47 % by volume;
O ₂ :	7.5 % by volume;
H ₂ O:	3 % by volume;
CO ₂ :	2.5 % by volume;

GHSV: 4000 standard l of gas/l of cat•h.

The N₂O conversions were calculated according to the following formula:

$$\text{Conversion in \%} = \frac{\text{Conc. of N}_2\text{O at the gas inlet} - \text{Conc. of N}_2\text{O at the gas outlet}}{\text{Conc. of N}_2\text{O at the gas inlet}} \times 100$$

30

The concentration of the N₂O was in each case

determined by gas chromatography.

Example 1

Production of the catalyst: 80 g of commercial aluminum oxide support (BASF D 10-11) (BET surface area 210 m²/g; water absorption 65.9% by weight, corresponding to a pore volume of 65.9 m²/g, the pore distribution is shown in Figure 1) was impregnated with 56 ml of an aqueous solution containing 22.24 g of AgNO₃, then allowed to stand for one hour at room temperature. The impregnated support was dried to constant weight at 120°C and finally calcined for 4 hours at 700°C. The catalyst thus obtained contained 14.2% by weight of silver and had a BET surface area of 163 m²/g. The crystallographic phase of the support was gamma-aluminum oxide. The silver particle size was 27 nm.

Over an operating time of 550 hours at a reactor inlet temperature of 550°C, the catalyst showed N₂O conversions of > 99%.

After the end of the test, the catalyst had a BET surface area of 130 m²/g. The sole crystallographic phase of the support at the end of the test was still gamma-aluminum oxide, the silver particle size was 32 nm after the test.

Example 2

Production of the catalyst: 126.75 g of commercial aluminum oxide support (BET surface area 157 m²/g; water absorption 61.3% by weight, for pore distribution see Figure 2) was impregnated with 94 ml of an aqueous solution containing 35.22 g of AgNO₃, then allowed to stand for one hour at room temperature. The impregnated support was dried to constant weight at 120°C and finally calcined for 4 hours at 700°C. The catalyst thus obtained contained 14.2% by weight of silver and had a BET surface area of 128 m²/g. The crystallographic phase of the support was gamma-aluminum oxide.

Over an operating time of 280 hours at a reactor inlet temperature of 532°C, the catalyst showed N₂O

conversions of > 99%.

After the end of the test, the catalyst had a BET surface area of $109 \text{ m}^2/\text{g}$, the crystallographic phase of the support was, as before, gamma-aluminum oxide.

5 Example 3

Production of the catalyst: 160.95 g of commercial aluminum oxide support (BET surface area $102 \text{ m}^2/\text{g}$; water absorption 38.7% by weight) was impregnated with 62.3 ml of an aqueous solution containing 44.71 g of AgNO_3 , then allowed to stand for one hour at room temperature. The impregnated support was dried to constant weight at 120°C and finally calcined for 4 hours at 700°C . The catalyst thus obtained contained 14.5% by weight of silver and had a BET surface area of $82 \text{ m}^2/\text{g}$.
15 The crystallographic phase of the support was delta-aluminum oxide.

Over an operating time of 250 hours at a reactor inlet temperature of 529°C , the catalyst showed N_2O conversions of > 99%.

20 After the end of the test, the catalyst had a BET surface area of $77 \text{ m}^2/\text{g}$, the crystallographic phase of the support was, as before, delta-aluminum oxide.

Example 4

Production of the catalyst: 225 g of $\text{AlO}(\text{OH})$ (Pural SB from Condea) were compounded with 25 g of $\text{Ce}_2(\text{CO}_3)_3$ and 12.5 g of formic acid for 5 hours, extruded, dried and calcined. 45.3 g of this material (BET surface area $185 \text{ m}^2/\text{g}$; water absorption 76% by weight) were impregnated with 36.7 ml of an aqueous solution containing 13.43 g of AgNO_3 , then allowed to stand for one hour at room temperature. The impregnated support was dried to constant weight at 120°C and finally calcined for 4 hours at 700°C to decompose the AgNO_3 to Ag. The catalyst thus obtained contained 14.3% by weight of silver and had a
30 BET surface area of $157 \text{ m}^2/\text{g}$.
35

Over an operating time of 350 hours at a reactor temperature of 524°C , the catalyst showed N_2O conversions

of > 99%.

After the end of the test, the catalyst had a BET surface area of 139 m²/g.

Example 5

5 Production of the catalyst: 225 g of AlO(OH) (as
in Example 4) were compounded with 25 g of La(NO₃)₃ and
12.5 g of formic acid for 3 hours, extruded, dried and
calcined. 64.10 g of this material (BET surface area
183 m²/g; water absorption 76% by weight) were impregnated
10 with 50.9 ml of an aqueous solution containing 17.8 g
of AgNO₃, then allowed to stand for one hour at room
temperature. The impregnated support was dried to constant
weight at 120°C and finally calcined for 4 hours at
700°C. The catalyst thus obtained contained 14.5% by
15 weight of silver and had a BET surface area of 156 m²/g.

Over an operating time of 280 hours at a reactor temperature of 530°C, the catalyst showed N₂O conversions of > 99%.

20 After the end of the test, the catalyst had a BET surface area of 136 m²/g.

Comparative Example 1

25 Production of the catalyst: 150 g of commercial aluminum oxide support (BET surface area 1.7 m²/g; water absorption 29.2% by weight) was impregnated with 100 ml
of an aqueous solution containing 41.7 g of AgNO₃, then
allowed to stand for one hour at room temperature. The
impregnated support was dried to constant weight at 120°C
and finally calcined for 4 hours at 700°C. The catalyst
thus obtained contained 14.6% by weight of silver and had
30 a BET surface area of 1.12 m²/g. The crystallographic phase of the support was alpha-aluminum oxide.

35 The catalyst first showed N₂O conversions of 97.5% over an operating time of 150 hours at a reactor temperature of 610°C. The conversion then dropped further
to 86.5% despite a temperature increase to 630°C.

Comparative Example 2

Production of the catalyst: a palladium catalyst on alpha-aluminum oxide as described, for example, in DE-A 35 43 640 was replicated. 200 g of alpha-aluminum oxide (BET surface area 20.2 m²/g) were impregnated with NaOH and dried at 120°C. This support was impregnated with 96 ml of an aqueous sodium tetrachloropalladate(II) solution containing 1.29 g of Pd, then allowed to stand for three hours at room temperature. The Pd²⁺-containing support was treated with hydrazine to reduce the Pd²⁺. The catalyst was subsequently washed free of chlorine and dried to constant weight at 120°C. The catalyst thus obtained contained 0.64% by weight of palladium.

The catalyst first showed N₂O conversions of 43.3% over an operating time of 112 hours at a reactor inlet temperature of 600°C. Raising the temperature to 640°C enabled the conversion to be increased to 66.5%.



We claim:

1. A process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, at from 200 to 1000°C over silver-containing supported catalysts, wherein the supported catalyst comprises from 0.1 to 40 % by weight of silver, based on the total catalyst, and an aluminum oxide support having mesopores and macropores and a BET surface area of from 26 to 350 m²/g.
2. A process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, as claimed in claim 1, wherein the BET surface area of the aluminum oxide support is from 40 to 300 m²/g.
3. A process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, as claimed in claim 1, wherein the aluminum oxide support is present in a crystallographically pure phase or in a mixed phase.
4. A process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, as claimed in claim 1, wherein the pore distribution in the aluminum oxide support is bimodal or trimodal.
5. A process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, as claimed in claim 1, wherein the aluminum oxide support comprises pure aluminum oxide or mixtures of aluminum oxide with other oxides.
6. A process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, as claimed in claim 5, wherein the other oxide(s) is or are present in amounts of from 0.01 to 50 % by weight, based on the weight of the support, and the other oxides are those of the alkali metals, the alkaline earth metals, the rare earth metals, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, B, Ge, Sn, Pb, P, Bi, and/or Si.
7. A process for the selective catalytic decomposition



of nitrous oxide, either in pure form or present in gas mixtures, as claimed in claim 5, wherein a spinel phase is present in the doped support.

- 5 8. A process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, as claimed in claim 1 or 5, wherein not only silver but also further active components, in particular Cu, Au, Pd and/or Pt, are applied to the support.
- 10 9. A process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, as claimed in claim 1, wherein the decomposition is carried out in the presence of from 0.01 to 50 % by volume of NO and/or NO₂, based on the total gas.
- 15 10. A process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, as claimed in claim 1, wherein the N₂O content of the gas mixture is from 0.01 to 50 % by volume.
- 20 11. A process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, as claimed in claim 9, wherein the gas mixture comprises not only N₂O and NO but also N₂, O₂, CO; CO₂, H₂O and/or noble gases.
- 25 12. A process for the selective catalytic decomposition of nitrous oxide, either in pure form or present in gas mixtures, as claimed in claim 1, wherein the gas mixture is a waste gas from the preparation of adipic acid using nitric acid.