

SILVER-CONTAINING ALUMINA SUPPORTED CATALYST, AND
THE CATALYTIC DECOMPOSITION OF DINITROGEN MONOXIDE
WHICH IS PURE OR PRESENT IN GAS MIXTURES

5 The present invention relates to a silver-containing alumina supported catalyst and to a process for the catalytic decomposition at elevated temperature of dinitrogen monoxide which is pure or present in gas mixtures.

10 The catalytic decomposition of dinitrogen monoxide (laughing gas) has been known for a long time and is described in numerous publications relating to kinetic investigations. As early as 1936, the decomposition of dinitrogen monoxide in quartz vessels in the absence and presence of various catalysts such as SiO_2 , platinum
15 foil, titanium dioxide, platinum black, Al_2O_3 , charcoal and thorium dioxide at various temperatures was investigated (Gmelins Handbuch der anorganischen Chemie, Stickstoff, 8th Edition, page 573 et seq.). Kinetic investigations on pure silver, on silver/gold and silver/calcium
20 alloys are described by K.E. Hayes, Cand. [sic] J. Chem. 37 (1959) 583. A review of the energies of activation for the decomposition of dinitrogen monoxide on oxide catalysts, especially on mixed oxides, is given by R. Larsson in Catalysis Today 4 (1989) 235-251.

25 Industrial interest in the decomposition of dinitrogen monoxide to nitrogen and oxygen was stimulated by the need of NASA to generate air for astronauts to breathe from an easily handled compound by decomposing ammonium nitrate via laughing gas into the elements
30 (Chem. Abstract [sic] (1965) 1481). The catalysts described as suitable were: platinum on various inorganic supports, rhodium on alumina, and oxides of nickel, cobalt and molybdenum.

35 Another industrial application is the disposal of anesthetic gases, eg. in operating theaters. A number of Japanese patents deals with this application. The following catalyst systems are proposed: active carbon (in JP 54/11090), elements of the iron group in combina-



tion with rare earth metals (JP 61/45487), platinum, palladium, rhodium, indium [sic] and/or ruthenium (JP 55/31463) and copper oxide, chromium oxide on alumina (JP 61/50650). Dinitrogen monoxide is usually decomposed
5 in a 1:1 mixture with air. JP 61/53142 describes the removal of dinitrogen monoxide from waste gases on oxides of cobalt, copper and manganese on γ -alumina.

DE-A 3 543 640 proposes palladium-containing catalysts for decomposing dinitrogen monoxide.

10 JP 63/07826 describes the removal of dinitrogen monoxide from waste gases on noble metals or the oxides thereof on γ -alumina supports. The N_2O concentration in the gas in the example is 26 ppm.

In all of the publications cited above, reaction
15 was carried out with mixtures of dinitrogen monoxide and air or oxygen. DE-A 3 543 640 also describes reaction of mixtures containing 430 ppm NO_x and 4 % water (gaseous) on palladium catalysts.

DE-A 40 29 061 describes silver-containing
20 alumina supported catalysts for decomposing dinitrogen monoxide, where the alumina has a BET surface area of from 5 to 25 m^2/g .

The non-prior-published application DE 41 28 629 likewise describes silver-containing alumina supported
25 catalysts for decomposing dinitrogen monoxide and having a BET surface area of from 26 to 350 m^2/g .

It is an object of the present invention to provide a process and a catalyst for the catalytic decomposition of dinitrogen monoxide which is pure or
30 present in gas mixtures, by means of which dinitrogen monoxide can be decomposed to the elements nitrogen and oxygen even in the presence of higher concentrations of nitrogen oxides and gases other than oxygen or nitrogen (especially offgases from adipic acid plants), it being
35 the intention that the catalyst has a higher activity than catalysts previously disclosed. Another problem to be solved is the selective breakdown of dinitrogen monoxide so that there is negligible decomposition of other nitrogen oxides to the elements.





We have found that this object is achieved by catalysts which, besides silver and alumina, contain copper oxide.

5 The present invention also relates to a process for the catalytic decomposition at elevated temperature of dinitrogen monoxide which is pure or present in gas mixtures on silver-containing alumina supported catalysts which, besides silver and alumina, contain copper oxide.

10 Surprisingly, the decomposition of N_2O on the catalysts according to the invention starts at a distinctly lower temperature than on known catalysts.

The advantage of the process according to the invention is, furthermore, that dinitrogen monoxide can be selectively decomposed to the elements nitrogen and
15 oxygen not only in extremely pure form but also in mixtures with oxygen or air and in mixtures with air containing large amounts of water and/or large amounts of nitrogen oxides (nitrogen monoxide, nitrogen dioxide) without breakdown of the higher nitrogen oxides. There is
20 no difficulty in decomposing dinitrogen monoxide to its elements in mixtures with, for example, up to 65 % nitrogen dioxide (NO_2) and/or 20 % water.

The catalysts according to the invention generally have a BET surface area of from 0.1 to 350 m^2/g .

25 The processes for preparing the support are known from the prior art. It has proven advantageous to impregnate an Al_2O_3 support with a soluble copper compound (eg. nitrate, sulfate, carboxylates etc.) and subsequently thermally decompose the anion to the oxide. Another
30 possibility would be to mix a copper compound with an aluminum compound (dry or in suspension, especially spray dried), to compact the material (eg. by kneading, with or without the addition of a suitable molding aid), to shape by extrusion, to dry and subsequently to calcine to form
35 the oxides. The calcination can be carried out at from 300 to 1150°C.

The silver can in principle be applied by any of the methods proposed in the literature for preparing silver catalysts (eg. D.I. Hucknall, Selective Oxidations



of Hydrocarbons, Academic Press, London (1974), page 6). It is advantageous to use methods in which the silver is applied to a support. For example, a suspension of freshly precipitated, thoroughly washed silver oxide (DE-B 12 11 607) or silver carbonate (US 3 043 854) can be applied to a support by rolling, and the silver compound can then be thermally decomposed to silver. The preferred method is to impregnate a large-pore support with the solution of a silver salt (eg. silver nitrate (US 3 575 888) or silver lactate (DE-B 12 11 607) or of a silver complex compound (eg. a silver amine [sic] carboxylate complex (DE-A 21 59 346) and subsequently to decompose the silver compound by treatment with a reducing agent or by heat.

Preferred catalysts according to the invention generally contain from 0.1 to 40 % by weight, in particular from 2 to 25 % by weight, of silver based on the weight of the support. Larger amounts of silver are of no interest for economic reasons.

The size of the silver particles in the unused catalyst is, in particular, from 0.1 to 200 nm, preferably from 1 to 100 nm, particularly preferably from 2 to 50 nm. The size of the silver particles can be determined by, for example, X-ray diffraction.

A suitable copper oxide is either Cu_2O or CuO or a mixture of the two.

The copper oxide and alumina can also be present in whole or in part in the form of the mixed phase CuAl_2O_4 .

The copper oxide content in the catalyst is preferably from 0.1 to 90 % by weight, in particular from 2 to 60 % by weight, based on the complete catalyst.

The support can contain copper oxide and alumina alone or can be doped with other elements. Doping of supports with high surface areas (especially alumina supports) increases the thermal stability of the support (eg. DE 3 403 328, DE 2 500 548, Appl. Catal. 7 (1983) 211-220, J. Catal. 127 (1991) 595-604). The foreign ions are also intended to contribute to the catalytic activity



of the catalyst. Compounds of the following elements can be used for the doping: alkali metals, alkaline earth metals, rare earth metals, metals in the first transition series, Y, Zr, B, Si and Zn. The content of doping compounds (promoters) in the alumina-containing catalyst can be from 0.01 to 50 % by weight.

Particularly suitable promoters are compounds of the elements Mg, Ca, Sr, Ba, Co, Ni, Fe, Y and Ce. ZnO is particularly preferred.

The porosity of the support is advantageously such that the pore volume is from 0.01 to 0.8 ml/g. The support advantageously contains meso- and/or macropores. Mesopores are defined as pores with a diameter of from 2 to 50 nm, and macropores are those with a diameter above 50 nm.

Besides silver, the catalyst can also contain other metallic active components, especially Au, Pd, Pt.

The supported catalysts according to the invention can be in the form of pellets, honeycombs, rings, chips, solid or hollow extrudates or in 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 the shape and size be chosen to minimize the pressure drop.

In the process according to the invention, dinitrogen monoxide or a gas mixture containing dinitrogen monoxide is passed at elevated temperature, preferably from 200°C to 900°C, over the supported catalyst and thus decomposed to nitrogen and oxygen. The GHSV (gas hour space velocity) can be from 500 to 50,000 l (STP) of gas/l of cat. ·h, preferably from 1500 to 20,000 l (STP) of gas/l of cat. ·h.

The process according to the invention can be carried out by preheating pure dinitrogen monoxide or gas mixtures or waste gas containing dinitrogen monoxide in an oven or heat exchanger to the required reactor [sic] temperature and then passing it through a tube packed with the catalyst according to the invention. The preheating of the reaction gas can also take place in the

tube by an upstream layer of inert material. The catalyst and/or the inert material can be heated not only by an external heat source but also by the heat liberated during the decomposition of the dinitrogen monoxide.

5 The gas mixture treated by the process according to the invention can, besides the N_2O , also contain, in particular, NO and/or NO_2 , in particular in an amount of from 0.01 to 50 % of the total gas volume. The NO_2 content in the gas mixture is preferably from 0.01 to 50 %
10 by volume, in particular from 0.1 to 30 % by volume. The gas mixture can, besides N_2O and NO/NO_2 (NO_x), also contain N_2 , O_2 , CO , CO_2 , H_2O and inert gases.

 The process is generally carried out in a pressure range from 0.1 to 20 bar, ie. under sub- or super-
15 atmospheric pressure. The pressure is preferably from atmospheric pressure to 7 bar.

 The process can be carried out either under adiabatic or under isothermal conditions.

 The catalyst according to the invention and the
20 process according to the invention are particularly suitable for decomposing N_2O in the offgases from the preparation of adipic acid, eg. by oxidation of cyclohexanol and/or cyclohexanone with nitric acid.

 A particular advantage of the process is that N_2O
25 is selectively decomposed, ie. there is no decomposition of NO_x which is the required product.

 The catalytic decomposition of dinitrogen monoxide, either pure or in gas mixtures, takes place at distinctly lower temperatures with the catalyst and
30 process according to the invention than in the prior art. The invention represents a distinct improvement both in economic terms and in respect of the catalyst performance.

EXAMPLES

35 Typical gas composition:

N_2O :	23 % by volume
NO_2 :	17 % by volume
N_2 :	47 % by volume
O_2 :	7.5 % by volume

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H₂O: 3 % by volume

CO₂: 2.5 % by volume

GHSV: 4000 l (STP) of gas/l of cat. ·h

The N₂O conversions were calculated by the following

5 formula:

$$\text{N}_2\text{O conc. at gas inlet} - \text{N}_2 \text{ conc. at gas outlet}$$

$$\% \text{ conversion} = \frac{\text{N}_2\text{O conc. at gas inlet}}{\text{N}_2\text{O conc. at gas inlet}}$$

- 10 The N₂O concentration was determined by gas chromatography in each case.

Preparation of the catalysts

EXAMPLE 1

- 270 g of AlO(OH) (Pural SB) were kneaded with
15 30 g of CuO and 10 g of formic acid (dissolved in 220 ml of H₂O) for 1 h, extruded, dried and calcined. 85.5 g of this (BET surface area 101 m₂/g [sic]; water uptake 52.7 % by weight) were impregnated with 45.19 ml of aqueous solution containing 23.8 g of AgNO₃ and then left
20 to stand at room temperature for one hour. The impregnated support was dried to constant weight at 120°C and finally calcined at 700°C for 4 h. The resulting catalyst contained 14.4 % by weight silver and had a BET surface area of 94 m²/g.

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EXAMPLE 2

- 83.1 g of commercial alumina support (BET surface area 157 m²/g; water uptake 63.85 % by weight) were impregnated with 53 ml of aqueous solution containing 28.1 g of Cu(NO₃)₂ and then left to stand at room temperature for one hour. The impregnated support was dried to constant weight at 120°C and finally calcined at 600°C for 4 h. The resulting support contained 10 % by weight CuO. 67.8 g of the copper oxide-containing alumina support were impregnated with 40.4 ml of aqueous solution
30 containing 18.9 g of AgNO₃ and then left to stand at room temperature for one hour. The impregnated support was
35

dried to constant weight at 120°C and finally calcined at 600°C for 4 h. The resulting catalyst contained 14.9 % by weight silver and had a BET surface area of 104 m²/g.

EXAMPLE 3

5 192.75 g of commercial alumina support (BET surface area 157 m²/g; water uptake 61.3 % by weight) were impregnated with 122 ml of aqueous solution containing 65.05 g of Cu(NO₃)₂·6H₂O and then left to stand at room temperature for one hour. The impregnated support
10 was dried to constant weight at 120°C and finally calcined at 600°C for 4 h.

73.58 g of the alumina support loaded with copper oxide were impregnated with 43 ml of aqueous solution containing 29.9 g of Zn(NO₃)₂·6H₂O and then left to stand
15 at room temperature for one hour. The impregnated support was dried to constant weight at 120°C and finally calcined at 600°C for 4 h. The resulting catalyst contained 9.8 % by weight CuO and 9.9 % by weight ZnO.

78.7 g of the alumina support containing copper
20 oxide and zinc oxide were impregnated with 37 ml of aqueous solution containing 21.9 g of AgNO₃ and then left to stand at room temperature for one hour. The impregnated support was dried to constant weight at 120°C and finally calcined at 600°C for 4 h. The resulting catalyst
25 contained 14.8 % by weight silver and had a BET surface area of 75.8 m²/g.

EXAMPLE 4

A mixture of 127.1 g of AlO(OH) (Pural SB), 252.0 g of thermally pretreated Al₂O₃ (Puralox SCF A230)
30 and 240.0 g of CuO was kneaded with the addition of 20 ml of concentrated formic acid in 210 ml of H₂O for 1 h, extruded, dried and calcined. The support contains [sic] 39.8 % by weight CuO. 59.1 g of this were impregnated with 29.5 ml of aqueous solution containing 16.4 g of
35 AgNO₃ and then left to stand at room temperature for one hour. The impregnated support was dried to constant weight at 120°C and finally calcined at 700°C for 4 h. The resulting catalyst contained 14.6 % by weight silver and had a BET surface area of 63 m²/g.





EXAMPLE 5

A mixture of 127.1 g of $\text{AlO}(\text{OH})$ (Pural SB), 252.0 g of Al_2O_3 as in Example 4 and 240.0 g of CuO was kneaded with the addition of 20 ml of concentrated formic acid in 210 ml of H_2O for 1 h, extruded, dried and calcined. The support contains [sic] 39.8 % by weight CuO .

49.5 g of this were impregnated with 32 ml of aqueous solution containing 78.8 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and then left to stand at room temperature for one hour. The impregnated support was dried to constant weight at 120°C and finally calcined at 700°C for 4 h.

61.1 g of this were impregnated with 27 ml of aqueous solution containing 17.0 g of AgNO_3 and then left to stand at room temperature for one hour. The impregnated support was dried to constant weight at 120°C and finally calcined at 700°C for 4 h. The resulting catalyst contains [sic] 15.0 % by weight silver and had a BET surface area of $65 \text{ m}^2/\text{g}$.

COMPARATIVE EXAMPLE 1

A catalyst was prepared as described in DE-A 40 29 061. 150 g of commercial alumina support (BET surface area $1.7 \text{ m}^2/\text{g}$; water uptake 29.2 % by weight) were impregnated with 100 ml of aqueous solution containing 41.7 g of AgNO_3 and then left to stand at room temperature for one hour. The impregnated support was dried to constant weight at 120°C and finally calcined at 700°C for 4 h. The resulting catalyst contained 14.6 % by weight silver and had a BET surface area of $1.12 \text{ m}^2/\text{g}$.

COMPARATIVE EXAMPLE 2

The palladium catalyst on alpha-alumina preferred according to DE-A 35 43 640 was prepared. 200 g of alpha-alumina (BET surface area $20.2 \text{ m}^2/\text{g}$) 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 g of Pd and then left to stand at room temperature for 3 hours. The Pd^{2+} -containing support was treated with hydrazine to reduce the Pd^{2+} . The catalyst was then washed until free of chlorine and dried to constant weight at 120°C . The resulting catalyst contained 0.4 % by weight palladium.



COMPARATIVE EXAMPLE 3

A catalyst was prepared as described in DE 41 28 629. 225 g of $\text{AlO}(\text{OH})$ (Pural SB) were kneaded with 25 g of $\text{La}(\text{NO}_3)_3$ and 12.5 g of formic acid for 3 h, extruded, dried and calcined. 64.10 g of this (BET surface area $183 \text{ m}^2/\text{g}$; water uptake 76 % by weight) were impregnated with 50.9 ml of aqueous solution containing 17.8 g of AgNO_3 and then left to stand at room temperature for one hour. The impregnated support was dried to constant weight at 120°C and subsequently calcined at 700°C for 4 h. The resulting catalyst contained 14.5 % by weight silver and had a BET surface area of $156 \text{ m}^2/\text{g}$.

Decomposition of dinitrogen monoxide

The test apparatus was a reaction tube made of Hasteloy C steel, 80 cm long, divided into heating and reaction zones. The internal diameter was 18 mm. In order to be able to measure the temperature profile in the tube, an inner tube which had an external diameter of 3.17 mm was used, by a thermal element being able easily to be moved. To improve heat transfer, the reactor was packed with inert material (steatite) in the heating zone. In each case, 40 ml of catalyst (1.5-2 mm chips) were tested under atmospheric pressure.

Test results

Catalyst	Running time (h)	Temperature ($^\circ\text{C}$)	Conversion (%)
1	164	520	> 99.9
2	242	490	> 99.9
3	124	500	> 99.9
4	150	500	> 99.9
5	240	495	> 99.9
C1	150	610	97.5
C2	112	640	66.5
C3	280	530	> 99.9

The results show that the catalyst according to

the invention gives high conversions although the reaction temperature is lower than with known catalysts. The tests also show that the catalysts according to the invention have a long useful life.

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We claim:

1. A silver-containing alumina supported catalyst for the decomposition of dinitrogen monoxide which is pure or present in gas mixtures, wherein the supported catalyst contains copper oxide besides silver and alumina.
2. A catalyst as claimed in claim 1, wherein the copper oxide content is from 0.1 to 90 % by weight.
3. A catalyst as claimed in claim 1, which contains at least one other promoter.
4. A catalyst as claimed in claim 3, wherein the promoter or promoters are selected from compounds of the following elements: alkali metals, alkaline earth metals, rare earth metals, metals of the first transition series, Y, Zr, B, Si and Zn.
5. A catalyst as claimed in claim 4, wherein the promoters are compounds of the elements Mg, Ca, Sr, Ba, Co, Ni, Fe, Y, Ce.
6. A catalyst as claimed in claim 4, which contains zinc oxide as additional promoter.
7. A catalyst as claimed in claims 3 to 6, which contains from 0.01 to 50 % by weight of promoters.
8. A catalyst as claimed in claim 1, wherein the porosity is from 0.01 to 0.8 ml/g.
9. A catalyst as claimed in claim 1, wherein mesopores and/or macropores are present.
10. A catalyst as claimed in claim 1 or 2, wherein copper oxide and alumina are present in whole or in part in the form of the mixed phase CuAl_2O_4 .
11. A catalyst as claimed in claim 1, wherein the silver content is from 0.1 to 40 % by weight.
12. A catalyst as claimed in claim 1, which contains other metals as active components.
13. A catalyst as claimed in claim 12, wherein the metallic active components are Au, Pd and/or Pt.
14. A process for the catalytic decomposition of dinitrogen monoxide which is pure or present in gas mixtures at elevated temperature on silver-containing alumina supported catalysts, wherein a supported catalyst



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as claimed in any of claims 1 to 13 is employed.

15. A process as claimed in claim 14, wherein the decomposition is carried out in the presence of from 0.01 to 65 % by volume nitrogen oxides (NO_x).

5 16. A process as claimed in claim 14, wherein the decomposition is carried out at from 200° to 900°C.

17. A process as claimed in claim 14, wherein the N_2O content in the gas mixture is from 0.01 to 65 % by volume.

10 18. A process as claimed in claim 14, wherein the gas mixture also contains N_2 , O_2 , CO , CO_2 , H_2O and/or inert gases besides N_2O and NO_x .

15 19. A process as claimed in claim 14, wherein the decomposition is carried out either under adiabatic or isothermal conditions.

20. A process as claimed in claim 14, wherein the gas mixture is offgas from the preparation of adipic acid using nitric acid.

20 21. The use of a supported catalyst as claimed in claims 1 to 13 for decomposing dinitrogen monoxide.

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