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(54) **PROCEDE POUR LA DECOMPOSITION DE L'AMMONIAQUE CONTENU DANS UN EFFLUENT GAZEUX**

(54) **PROCESS FOR DECOMPOSING AMMONIA IN AN OFF-GAS**

(57) An improvement is provided in a process for the catalytic, low temperature oxidation of ammonia with oxygen to nitrogen in an ammonia-containing off gas at a temperature of between 200°C and 500°C. The improvement includes the first step of sulphating a catalyst which may be one of the following three alternative catalysts: two components, one component comprising at least one oxide of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, manganese and mixtures thereof, and a further component which is selected from the group consisting of the platinum metals, both such components being on an inert carrier; two components, one component comprising at least one sulphate of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, and manganese, and mixtures thereof, and a further component which is selected from the group consisting of the platinum metals, both such components being on an inert carrier; and three components, one component comprising at least one oxide of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, and manganese and mixtures thereof, a second component comprising at least one sulphate of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, and manganese, and mixtures thereof, and a further component which is selected from the group consisting of the platinum metals, all such components being on an inert carrier. The next step comprises contacting the ammonia-containing off-gas with the sulphated catalyst. The third step comprises withdrawing a decomposed gas therefrom which is rich in nitrogen.

ABSTRACT

An improvement is provided in a process for the catalytic, low temperature oxidation of ammonia with oxygen to nitrogen in an ammonia-containing off-gas at a temperature of between 200°C and 500°C. The improvement includes the first step of sulphating a catalyst which may be one of the following three alternative catalysts: two components, one component comprising at least one oxide of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, manganese and mixtures thereof, and a further component which is selected from the group consisting of the platinum metals, both such components being on an inert carrier; two components, one component comprising at least one sulphate of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, and manganese, and mixtures thereof, and a further component which is selected from the group consisting of the platinum metals, both such components being on an inert carrier; and three components, one component comprising at least one oxide of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, and manganese and mixtures thereof, a second component comprising at least one sulphate of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, and manganese, and mixtures thereof, and a further component which is selected from the group consisting of the platinum metals, all such components being on an inert carrier. The next step comprises contacting the ammonia-containing off-gas with the sulphated catalyst. The third step comprises withdrawing a decomposed gas therefrom which is rich in nitrogen.

a) TITLE OF THE INVENTION

PROCESS FOR DECOMPOSING AMMONIA IN AN OFF-GAS

b) TECHNICAL FIELD TO WHICH THE INVENTION RELATES

The present invention is directed to a process for decomposing ammonia, and more specifically, to a process for the selective decomposition of ammonia to nitrogen in an ammonia-containing off-gas at low temperatures in the presence of a catalyst.

c) BACKGROUND ART

Catalytic decomposition of ammonia with oxygen to nitrogen and water proceeds according to the following reaction:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

In addition to the above-depicted oxidation reaction, ammonia further reacts with oxygen to form nitrogen oxides, mainly by the reactions:

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$$

For reasons of high formation of desired nitrogen, the process depends substantially on the selectivity of a decomposition catalyst for the formation of nitrogen as the main oxidation product rather than the undesired nitrogen oxides.

Known catalysts which are active for the selective decomposition of ammonia are cobalt or cobalt-oxide containing catalysts, as described in German Offenlegungsschrift No. 2,026,657, and vanadium oxide-containing catalysts which are supported on a carrier of alumina, as disclosed in US Patent No. 5,139,756. Other known catalysts for the decomposition of ammonia in the lower temperature range contain platinum metals (German Offenlegungsschrift No. 2,447,552).

d) DESCRIPTION OF THE INVENTION

It has now been found that selectivity and activity of the known ammonia decomposition catalysts are, surprisingly, improved when sulphating the catalysts during, or prior to, contact with the ammonia-containing gas.

In accordance with the above findings and observations, this invention provides a process for the catalytic, low temperature oxidation of ammonia with oxygen to nitrogen in an ammonia-containing off-gas that also contains an oxygen-containing gas, at a temperature of between 200°C. and 500°C., the improvement comprising the first step of: sulphating a catalyst comprising: two components, one component comprising at least one oxide of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, manganese and mixtures thereof, and a further component which is selected from the group consisting of the platinum metals, both such components being on an inert carrier; two components, one component comprising at least one sulphate of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, and manganese, and mixtures thereof, and a further component which is selected from the group consisting of the platinum metals, both such components being on an inert carrier; or three components, one component comprising at least one oxide of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, and manganese and mixtures thereof, a second component comprising at least one sulphate of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, and manganese, and mixtures thereof, and a further component which is selected from the group consisting of the platinum metals, all the components being on an inert carrier. The next step involves contacting the ammonia-containing off-gas with the sulphated catalyst. The next step involves withdrawing a decomposed gas therefrom which is rich in nitrogen.

By one variant thereof, the ammonia-containing off-gas also contains O_2.

By a second variant thereof, and/or the above variant, the platinum metal comprise at least one of platinum and palladium.

By a third variant thereof and/or the above variants, the catalyst comprises the platinum metal in an amount of 1-20% by weight, calculated as the total weight of the catalyst.

By a fourth variant thereof, and/or the above variants, the catalyst contains the further component in an amount of 100ppm-2000ppm by weight, calculated on the total weight of the catalyst.

By a fifth variant thereof, and/or the above variants, the inert carrier is selected from the group of alumina, titania, and silica, and mixtures thereof.

By a sixth variant thereof, and/or the above variants, the catalyst is in the shape of rings, pellets, tablets or monolithic structured bodies.

By a seventh variant thereof, and/or the above variants, the catalyst is sulphated by adding a volatile sulphur compound to the off-gas. By a variation thereof, the volatile sulphur compound is added in an amount of between 1ppm-4000ppm by volume to the off-gas.

By an eighth variant thereof, the oxidation of ammonia to nitrogen is substantially complete.

In carrying out such process industrially, the catalysts will typically comprise the active catalytic metal in an amount of 1%-20% by weight and a platinum metal promoter in an amount of 100ppm-2000ppm by weight, which is supported on the carrier. Suitable carriers may be alumina, titania, or silica, or mixtures thereof.

The catalysts are preferably used in the shape of rings, pellets, tablets and monolithic structured bodies.

Convenient procedures for manufacturing the catalysts for use in the process of aspects of this invention comprise the steps of impregnating the carrier material with an aqueous solution of a salt of the active compounds, and then heating to a temperature which is sufficient to decompose the salt to the oxide or sulphide of the metal component.

As mentioned before, the activity and the selectivity of the catalysts during the decomposition of ammonia is considerably increased, when the catalysts are used in their sulphated form. To maintain the catalysts in the sulphated form, volatile sulphur compounds in an amount, typically of 1-4000 ppm are, preferably, added to the ammonia-containing gas prior to contact with the catalysts.

By the process of broad aspects of this invention, an off-gas, having ammonia in a concentration of up to 10.000 ppm by volume, is contacted with the above catalysts usually arranged in a reactor as a fixed bed. At an inlet temperature of between 200°C and 500°C, preferably 230-380°C, ammonia decomposition to nitrogen is substantially complete.

e) AT LEAST ONE MODE FOR CARRYING OUT THE INVENTION

Example 1

Preparation of Co/Pt catalyst supported on a silica carrier.

A silica carrier in the form of a ring with an outer diameter of 10 mm was calcined at 600°C in air.

The calcined carrier was then impregnated with an aqueous solution of $Co(NO_3)_2$ to a final cobalt concentration of 10% by weight calculated on the total weight of the impregnated carrier. The carrier was dried after impregnation. In a subsequent step, the carrier was further impregnated with platinum from an aqueous solution of H_2PtCl_6 to a final load of Pt of 670 ppm by weight calculated on the total weight of the impregnated carrier. Finally, the impregnated carrier was dried and calcined at 500°C in air to obtain the active catalyst.

Example 2

In a procedure which is similar to that of Example 1, a catalyst was prepared having 10% by weight Cu and 670 ppm by weight Pt as the active material on a silica carrier.

The calcined carrier was impregnated with an aqueous solution of $Cu(No_3)_2$, and, subsequently, with an aqueous solution of H_2PtCl_6. The impregnated carrier is then calcined as described in Example 1.

Example 3

Preparation of catalyst having Cu, Ni and Pt as active material on a silica carrier.

The catalyst was prepared at a procedure similar to the one of Example 2 except for an additional step of impregnating the carrier with an aqueous solution of $Ni(NO_3)_2$ to a final load of Ni of 10% by weight before impregnation with platinum.

Example 4

Preparation of a catalyst having Cu, Pd and Pt as active material on a silica carrier.

A calcined silica carrier as described above was impregnated with an aqueous solution of $Cu(NO_3)_2$ to a final load of Cu of 10% by weight.

The Cu-impregnated carrier was dried and then impregnated with Pd and Pt from an aqueous solution of $Pd(NO_3)_2$ and H_2PtCl_6, each to a content of 670 ppm by weight calculated on the total weight of the impregnated carrier. Finally, the impregnated catalyst was activated by calcination at 500°C in air.

Example 5

The catalysts, as prepared in Example 1-4, were tested for their activity and selectivity in the decomposition of ammonia to nitrogen.

Samples of 0.25 litre were loaded as fixed bed in an adiabatic operated reactor tube. A gas with the composition of

20 vol% O_2
2 vol% H_2O
1000 ppm NH_3, and

a sulphur dioxide content as specified in the Table below was passed under the conditions specified in the Table

through the reactor. Ammonia conversion rates and selectivity for nitrogen obtained with the catalysts under the specified conditions are summarized in the Table.

Catalyst concentration	Temp °C Inlet	Gas Flow NHSV $Nm^3/m^3/h$	SO_2-concentration Inlet ppm	NH_3-concentration		N_2 selectivity %
				Inlet ppm	Conv.-outlet %	
Co/Pt	232	10000	0	1000	94	53
	292	10000	200	1000	92	77,9
Cu/Pt	290	10000	0	1000	92	26,1
	293	10000	10	1000	98	95,7
	293	10000	200	1000	92	97
	330	10000	200	1000	99,8	90,9
Cu/Ni/Pt	290	10000	0	1000	95	45,3
	306	10000	200	1000	96	98,8
Cu/Pd/Pt	290	10000	0	1000	95	38,9
	328	10000	200	1000	99,6	99,1

As obvious from the results, decomposition of ammonia to nitrogen is considerable improved in the presence of small amounts of sulphur dioxide added to the test gas at the reactor inlet. When compared to the known processes operating with non-sulphated catalysts, the presence of sulphur in the gas results in a high selectivity during decomposition of ammonia to nitrogen. Formation of noxious nitrogen oxides, as with the known catalytic ammonia decomposition processes substantially depressed.

CLAIMS

1. In a process for the catalytic low temperature oxidation of ammonia with oxygen to nitrogen in an ammonia-containing off-gas that also contains an oxygen-containing gas, at a temperature of between 200°C. and 500°C., the improvement comprising the steps of:

(A) sulphating a catalyst comprising:

(i) two components, one component comprising at least one oxide of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, manganese and mixtures thereof, and a further component which is selected from the group consisting of the platinum metals, both said components being on an inert carrier;

(ii) two components, one component comprising at least one sulphate of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, and manganese, and mixtures thereof, and a further component which is selected from the group consisting of the platinum metals, both said components being on an inert carrier; or

(iii) three components, one component comprising at least one oxide of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, and manganese and mixtures thereof, a second component comprising at least one sulphate of a metal which is selected from the group consisting of copper, cobalt, iron, chromium, nickel, and manganese, and mixtures thereof, and a further component which is selected from the group of platinum metals, all said components being on an inert carrier;

(B) contacting said ammonia-containing off-gas with said sulphated catalyst; and

(C) withdrawing a decomposed gas therefrom which is rich in nitrogen.

2. The process according to claim 1 wherein said ammonia-containing off-gas also contains O_2.

3. The process according to claim 1 or claim 2, wherein said platinum metals comprise at least one of platinum and palladium.

4. The process according to claim 1, claim 2 or claim 3, wherein said catalyst comprises said metal in an amount of 1%-20% by weight, calculated as the total weight of said catalyst.

5. The process according to claims 1 to 4, wherein said catalyst comprises said further component in an amount of 100ppm-2000ppm by weight, calculated on the total weight of said catalyst.

6. The process according to claims 1 to 5, wherein said inert carrier is selected from the group of alumina, titania, and silica, and mixtures thereof.

7. The process according to claims 1 to 6, wherein said catalyst is in the shape of rings, pellets, tablets or monolithic structured bodies.

8. The process according to claims 1 to 7, wherein said catalyst is sulphated by adding a volatile sulphur compound to said off-gas.

9. The process according to claim 8, wherein said volatile sulphur compound is added in an amount of between 1ppm-4000ppm by volume to said off-gas.

10. The process according to claims 1 to 9, whereby the oxidation of ammonia to nitrogen is substantially complete.