PATENT SPECIFICATION (11) 1 599 079

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(21) Application No. 25185/78 (22) Filed 31 May 1978 (19)
(31) Convention Application No. 52/067584 (32) Filed 8 Jun. 1977 in
(33) Japan (JP)
(44) Complete Specification Published 30 Sep. 1981
(51) INT. CL.^{3} B01D 53/36
(52) Index at Acceptance
C1A S21X S21Y S410 S411 S41Y S491
S60Y S611 S616 S683 SA

THE PATENT OFFICE
LONDON

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(54) METHOD FOR REMOVAL OF NITROGEN OXIDES FROM EXHAUST GASES

(71) We, KUREHA KAGAKU KOGYO KABUSHIKI KAISHA, a company organised under the laws of Japan, of No. 8, Horidome-cho 1-chome, Nihonbashi, Chuo-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a method for removing nitrogen oxides (hereinafter referred to as NO_X) from an exhaust gas containing NO_X, by contacting the exhaust gas with ammonia in the presence of a catalyst.

Various methods have been heretofore suggested for the removal of NO_X from NO_X-containing exhaust gases such as those issuing from combustion sources. Among these methods, one involves reduction of NO_X to nitrogen using ammonia as the reducing agent and this method is considered to be highly promising because it is effective even for the treatment of exhaust gases containing NO_X and oxygen in relatively high concentrations. This method usually involves contacting the exhaust gas containing NO_X with ammonia at a temperature of from 200°C to 400°C in the presence of a catalyst so that the NO_X reacts with ammonia and is converted into N_2. The principle reduction reactions involved in this method may be represented by the following formulae:

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

Various catalysts for this reduction process have been suggested, including platinum-based catalysts, iron-based catalysts, copper-based catalysts, and manganese dioxide-based catalysts. Of these catalysts, those based other than on platinum and manganese dioxide are generally deficient in activity at relatively low temperatures, say below 200°C. Platinum-based catalysts, on the other hand, have the disadvantage that, as the process of reduction progresses, they are liable to be gradually poisoned by sulfur oxides (hereinafter referred to as SO_X) usually present in the exhaust gas under treatment, and, moreover, the range of temperatures at which they exhibit high activity is narrow. Furthermore, platinum-based catalysts are expensive. Known manganese dioxide-based catalysts (such as disclosed, for example, in Japanese Patent Laid-Open Publication No. 17368/1975) are relatively dense in structure and have thus few surface pores. Accordingly their catalytic activity considerably decreases with increasing size of the particles of the catalyst but even if these manganese dioxide-based catalysts are used in the form of very small particles they exhibit only moderate activity at temperatures below 200°C.

Thus, it is difficult to maintain a high rate of NO_X- removal when an NO_X-containing exhaust gas is treated at a temperature of not more than 200°C using the catalysts discussed above.

We have now found, in accordance with the present invention, that NOx may be satisfactorily reduced with ammonia at temperatures below 200°C using as catalyst a specific manganese oxide product.

Thus, the present invention provides a method for removing nitrogen oxides from an exhaust gas by contacting the exhaust gas with ammonia, wherein the exhaust gas is contacted with ammonia at a temperature not greater than 200°C in the presence of a catalyst comprising manganese oxide of the formula MnOx, wherein x is at least 1.5 and a binder which is alumina or silica gel, said catalyst having a specific surface area of not less than 80 m^2/g and a pore volume of pores with a radius of above 40Å of above 0.2ml/g, and being obtained by heating a mixture of manganese carbonate and a binder which is alumina sol or silica sol at a temperature of from 200° to 500° for from 2 to 24 hours in a gaseous atmosphere containing not less than 1% by volume of oxygen.

The catalyst used in the present invention is a manganese oxide product of a specific type. Specifically, the manganese oxide catalyst is obtained by mixing manganese carbonate (for example, in the form of a powder) with a binder which is alumina sol or silica sol, and after shaping this mixture into a desired form if required, heating the mixture of manganese carbonate and binder at a temperature of from 200° to 500° in a gaseous atmosphere which contains not less than 1% by volume, preferably not less than 10% by volume, of oxygen, for from 2 to 24 hours.

As previously indicated, the thermal treatment employed in the preparation of the catalyst is conducted in a gas atmosphere containing not less than 1% by volume of oxygen. If the oxygen content of the gas is less than 1% by volume, oxidation will become unsatisfactory, making it difficult to produce an active catalyst. Examples of oxygen-containing gases suitable for the thermal treatment are a combustion exhaust gas (which is preferred to be free of SO_X to avoid poisoning of the final catalyst) obtained by combusting a liquefied natural gas; air; pure oxygen; oxygen-containing steam; and an oxygen-containing inert gas (such as a mixed gas of nitrogen and oxygen). Of these, the combustion exhaust gas or air are preferred from the viewpoint of economy.

Expressing the manganese oxide product as MnO_X, the thermal treatment is effected until a product corresponding to $x \geqq 1.5$, preferably $x \geqq 1.7$, is obtained. In this connection it will be noted that the manganese oxide product is considered to be a mixture of MnO, MnO_2, Mn_2O_3 and Mn_3O_4 and thus the atomic ratio of *Mn* to *O* is not generally a whole integer. The thermal treatment should be effected at a temperature of from 200° to 500°C for below 200°C the decomposition or oxidation of manganese carbonate will not proceed satisfactorily, whereas above 500°C manganese oxides of lower catalytic activity are produced in increasing amount. Preferably, the thermal treatment is conducted at a temperature of from 250°C to 350°C.

The manganese oxide product thus obtained is relatively porous, having a specific surface area above 80 m^2/g. In addition, the product has relatively large-sized pores, with a pore volume of pores with a radius above 40 Å of above 0.2 mℓ/g. As will be appreciated from the above data, such a manganese oxide catalyst having not only a high specific surface area but also relatively large-sized pores, allows diffusion of the exhaust gas being treated into the inside thereof, so that a large surface area of the product is effectively used, ensuring a good rate of NO_X-removal. Since such manganese oxide catalyst has both fine and relatively large pores, it can be used in moulded forms of a larger size than is usually the case; previously known catalysts for reducing NO_X have generally been used in forms having sizes of about 1 to 3 mm, whereas the catalyst used in preferred embodiments of the present invention can exhibit a high rate of NO_X-removal even when employed as a molding having a size above 4mm. For example, we have made catalysts which when shaped into a cylindrical form having a diameter of about 6 mm and a length of about 10 mm ensure a rate of NO_x-removal of above 98%

The invention is illustrated by the Example which follows:

Example

3 parts by weight of colloidal silica as SiO_2 was added to 100 parts by weight of manganese carbonate powder having a particle size of 1 to 1.5μ, to which was added water for kneading. The mixture was then extrusion molded and dried at 120°C to obtain cylindrical moldings each having a diameter of 7 mm and a length of about 13 mm. The moldings were thermally treated at 350°C for 7 hours while passing air sufficiently to give a catalyst. The catalyst had a manganese oxide composition of $MnO_{1.80}$ and a specific surface area of 158 m^2/g. The measurement of a pore distribution by a pressurized mercury method revealed that the catalyst had pores in radius ranges of 40 - 200 Å, 200 - 1000 Å and above 1000 Å and that capacities of the pores in such ranges were 0.18 mℓ/g, 0.02 mℓ/g and 0.27 mℓ/g, respectively.

When the catalyst thus obtained was used for treatment by passing therethrough an N_2 gas containing 500 ppm of NO, 500 ppm of NH_3, 3 % by volume of O_2 and 15 % by volume of H_2O at a space velocity of 10,000 hr^{-1}, the rates of removal of NO at reaction temperatures of 130°C, 150°C and 200°C were found to be 95 %, 98 % and 99 %, respectively.

WHAT WE CLAIM IS:

1. A method for removing nitrogen oxides from an exhaust gas by contacting the exhaust gas with ammonia, wherein the exhaust gas is contacted with ammonia at a temperature not greater than 200°C in the presence of a catalyst comprising manganese oxide of the formula MnO_x, wherein x is at least 1.5, and a binder which is alumina or silica gel, said catalyst having a specific surface area of not less than $80m^2/g$ and a pore volume of pores with a radius of above 40Å of above 0.2 ml/g, and being obtained by heating a mixture of manganese carbonate and a binder which is alumina sol or silica sol at a temperature of from 200° to 500°C for from 2 to 24 hours in a gaseous atmosphere containing not less than 1% by volume of oxygen.

2. A method according to Claim 1, wherein x is at least 1.7.

3. A method according to Claim 1 or Claim 2, wherein said gaseous atmosphere contains at least 10% by volume of oxygen.

4. A method according to any preceding claim, wherein said catalyst has been obtained by heating said mixture of manganese carbonate and binder at a temperature of from 250° to 350°C.

5. A method for removing nitrogen oxides from an exhaust gas, according to Claim 1 and substantially as described in the Example herein.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1981.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.