

A METHOD FOR REDUCING THE AMOUNT OF NO_x FROM FLUE GAS

Field of the invention

- 5 The present invention relates to a method for reducing the amount of nitrogen oxides (NO_x) emissions from pollution sources, such as combustion systems. More particularly, the present invention relates to a method for reducing NO_x from exhaust gas (for example, flue gas).

10 Background of the invention

One of the major problems in industrialised society is the production of air pollution from numerous sources. Air pollution can take various forms. Some of the different types of air pollutants include particulate emissions such as coal ash, partially burned coal particles, and
15 the like, including emissions of nitrogen oxides (commonly referred to collectively as "NO_x"). Pollution sources include automobiles, industrial plants, small commercial establishments, such as dry cleaners and service stations, and even nature itself.

Combustion effluents and waste products from particular types of sources have proven to be
20 major contributors to damaging air pollution when the effluents are discharged into the atmosphere. Unless these waste products are treated before their release into the atmosphere, serious smog and air pollution problems are encountered. It will be appreciated that high concentrations of air pollutants have serious deleterious impacts on the health and general welfare of society. Air pollution is known to aggravate certain medical conditions
25 (such as heart and lung problems) and is known to cause problems in the environment, ranging from corrosion to acid rain.

One of the most common components found in polluted air is nitrogen dioxide ("NO₂") which is known to be toxic. Nitrogen dioxide, which is brown in color, undergoes a series of
30 reactions, known generally as "photochemical smog formation," in the presence of sunlight and airborne hydrocarbons. These reactions result in a marked decline in overall air quality.

While NO₂ is produced from a wide variety of pollution sources, its primary source is from nitric oxide ("NO") released into the air. NO is commonly formed during combustion
35 processes, including internal combustion engines in automobiles, hydrocarbon fuel power plants, process furnaces, incinerators, coal-fired utility boilers, glass furnaces, cement kilns, oil field steam generators, gas turbines, and other similar installations.

There have been considerable efforts in the art to find effective ways to remove oxides of nitrogen from waste gases so that these waste gases may be discharged to the atmosphere without harm to the environment. NO_x reduction processes often teach the removal of NO_x from flue gases by reduction of the NO by the addition of ammonia, urea, or ammonia precursors, alone or in combination with some other combustional material, while the waste gas is at a relatively high temperature (generally from about 700°C to about 1200°C).

An example would be the use of the Selective Catalytic Reduction (SCR) process of converting nitrogen oxides (NO_x), in the presence of a catalyst, into molecular nitrogen, N₂ and water vapour. A reducing agent, such as urea, is added in a known SCR process. The volume of reducing agent is one of the factors that limits the NO_x removal efficiency. The higher the volume, the higher the operating costs. Thus, what is needed is a method that eliminates the use of a reducing agent, and combines the activation of a catalyst and removal of NO_x into a single step in a reactor and operates at a lower temperature.

Summary of the invention

In accordance with a preferred aspect of the present invention, there is provided a method for reducing the amount of NO_x in a flue gas, the method comprising: (a) reacting the NO_x with a catalyst at a temperature between 120°C to 200°C; and (b) discharging the flue gas containing a reduced amount of NO_x to the atmosphere; wherein the catalyst is contained within a fluidised bed reactor.

Preferably, the method further comprises precipitating the catalyst prior reacting it with the NO_x in the flue gas.

Preferably, the catalyst is a rare earth metal oxide. More preferably, the catalyst is cerium dioxide. The catalyst may be prepared by mixing a cerium salt and an alkali. The cerium salt may be cerium nitrate and the alkali may be any alkali selected from the group consisting of: sodium hydroxide, hexamethylenetetramine and ammonium hydroxide.

Preferably, the cerium dioxide is doped with 0.5mol% to 20mol% copper oxide and/or zirconium dioxide based on the weight of cerium dioxide.

Preferably, the catalyst is present in powder form. Preferably, the particle size of the catalyst is between 5.5nm to 30nm.

Preferably, the flue gas is introduced into the reactor at a flow rate from 25L/h.

Preferably, the concentration of NO_x in the flue gas is 200ppm.

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Preferably, the method further comprises reacting the NO_x with the catalyst in the presence of a balance gas. More preferably, the balance gas is argon. Still more preferably, the concentration of argon present in the flue gas is 200ppm.

10 Preferably, 83% of the NO_x in the flue gas is removed.

Brief description of figures

15 In order that the present invention may be fully understood and readily put into practical effect, there shall now be described by way of non-limitative examples only preferred embodiments of the present invention, the description being with reference to the accompanying illustrative figures.

In the Figures:

Figure 1 is a flow diagram of the method in accordance with the present embodiment;

20 Figure 2 is a schematic diagram of a method for preparing a catalyst in accordance with the present embodiment;

Figure 3 is a flow diagram of a method for preparing a catalyst in accordance with the present embodiment;

25 Figure 4 is a schematic diagram of a SCR reactor in accordance with the present embodiment;

Figure 5 is an image taken of catalyst, Lab-Ce-01, before being loaded into the reactor;

Figure 6 is an image taken of catalyst, Lab-Ce-01, after a test in the reactor;

Figure 7 is bar chart illustrating the average percentage of NO removed by catalyst, Lab-Ce-01, at 50-minutes intervals; and

30 Figure 8 is a bar chart illustrating the average percentage of NO₂ removed by catalyst, Lab-Ce-01, at 50-minutes intervals.

Detailed description of the preferred embodiments

Referring to Figure 1, a flow diagram of the method in accordance with the present embodiment is provided. The catalyst is prepared prior to reacting it with the NO_x in the flue gas.

Referring to Figure 2, a schematic diagram of a method for preparing a catalyst in accordance with the present embodiment is shown. The metal oxide catalysts may be prepared by a precipitation process. A cerium (III) salt is added into a mixing tank containing an alkali. Suitable alkalis include sodium hydroxide, hexamethylenetetramine and ammonium hydroxide. The mole ratio of cerium (III) salt to alkali may range from 1:1 to 1:40. Preferably, the cerium (III) salt is 0.5M to 2M cerium (III) nitrate.

Alternatively, the metal oxide catalysts may be prepared by a co-precipitation process. In addition to the cerium (III) salt and alkali, the mixture may include dopants' salt precursors such as copper (II) nitrate and/or zirconyl nitrate hydrate. The weight percentage of dopants (based on the weight of cerium dioxide) may range from 0.5% to 20%.

A capping agent may be added to the mixture for better particle size control. A suitable capping agent is sugar.

Referring to Figure 3, a flow diagram of a method for preparing a catalyst in accordance with the present embodiment is shown. The mixture is stirred under a predetermined constant speed, temperature and time. Upon precipitation and/or co-precipitation, the metal oxide catalysts are isolated, washed and dried at 60°C for a predetermined period of time. The time taken to prepare the metal oxide catalysts by precipitation and/ or co-precipitation may be between 2 to 4 hours.

Unlike known SCR processes, subsequent heat treatment, such as calcination or annealing to convert the metal oxide catalyst into an active catalyst, is not required as this step will take place in the SCR reactor.

The metal oxide catalysts are loaded into the SCR reactor, where the temperature of the reactor is adjusted to a predetermined temperature. The catalysts are calcined in the reactor at the predetermined temperature. An optimal temperature range for calcination of the catalysts may be between 120°C to 200°C.

Referring to Figure 4, a schematic diagram of a SCR reactor in accordance with the present embodiment is shown. A gas stream, such as flue gas, is introduced into the reactor when the predetermined temperature is maintained in the reactor. The gas stream may be pre-blended with a balance gas prior to being introduced into the reactor. The balance gas is preferably argon. A Venturi gas mixer may be employed to ensure a quick and good mixing of the gases. The balance gas keeps NO_x at a concentration of 200ppm in the reactor. The gas stream/argon mixture may be 200ppm NO, 200ppm NO_2 or 200ppm NO_2/NO . If NO_2/NO gas stream is used, the mole ratios of NO_2 to NO may be 3:1, 2:1, 1:1, 1:2 or 1:3. Preferably, the NO_2/NO ratio is 2:1 for optimal removal of NO_x in the reactor.

The pre-blended gas may be pre-heated in pre-heating tubes to a predetermined temperature before entering the reactor. An optimal temperature range for pre-heating the pre-blended gas may be between 120°C to 200°C.

The pre-blended, pre-heated gas stream may be introduced into the reactor at a flow rate from 25L/h.

Referring to Figure 5, an image of catalyst, Lab-Ce-01, before being loaded into the reactor is shown. The metal oxide catalysts in the reactor are present in powder form and form a catalyst bed. The flow of the gas stream fluidises the catalyst bed. Fluidisation of the catalyst bed converts the catalysts into more active compounds which will in turn catalyse the removal of NO_x .

Referring to Figure 6, an image of catalyst, Lab-Ce-01, after a test in the reactor is shown. Fluidisation of the catalyst bed advantageously prevents the aggregation of catalysts under the predetermined temperature, hence prolonging the use of catalysts. This is because fluidisation of the catalyst bed enables the catalysts to stay as nanopowder and/or submicron powder. Preferably, the particle size of the catalyst is between 5.5nm to 30nm.

The activated catalyst adsorbs the NO_x present in the gas stream and reduces the NO_x . The effectiveness of the catalysts is indicated by the data gathered by several experiments conducted on selected catalysts such as Lab-Ce-01, Lab-Ce-2 and Lab-Ce-03. Table 1 illustrates the effectiveness of the catalysts on the removal of NO, while Table 2 illustrates the effectiveness of the catalysts on the removal of NO_2 .

Removal of NO in SCR (experiments are conducted on NO gas only; initial concentration of NO = 200pm)			
Sample	Average amount of NO removed	% of NO removed	Temperature (SCR)
CeO ₂ (99.9% purity, 5um powder, Alfa Aesar)	30ppm (for 4h)	15%	120°C
Lab-Ce-01	50ppm (for 2h)	25%	120°C
Lab-Ce-02	75ppm (for 2h)	37.5%	120°C
CeO ₂ (99.9% purity, 5um powder, Alfa Aesar)	40ppm (for 4h)	20%	150°C
CeO ₂ (99.9% purity, 5um powder, Alfa Aesar)	17ppm (for 4h)	8.5%	200°C
Lab-Ce-01	100ppm (for 1h)	50%	200°C
Lab-Ce-02	150ppm (for 1h)	75%	200°C

Table 1: Data on Effectiveness of Catalysts on Removal of NO

Removal of NO ₂ in SCR (experiments are conducted on NO ₂ only; initial concentration of NO ₂ = 200pm)			
Sample	Average amount of NO ₂ removed	% of NO ₂ removed	Temperature (SCR)
CeO ₂ (99.9% purity, 5um powder, Alfa Aesar)	50ppm (for 1h)	25%	120°C
Lab-Ce-01	105ppm (for 1h)	52.5%	120°C
Lab-Ce-02	137ppm (for 1h)	68.5%	120°C
Lab-Ce-03	107ppm (for 1h)	53.5%	120°C
Lab-Ce-doped -01	147ppm (for 1h)	73.5%	120°C
Lab-Ce-01	166ppm (for 5h)	83%	150°C
CeO ₂ (99.9% purity, 5um powder, Alfa Aesar)	15ppm (4h)	7.5%	200°C
Lab-Ce-01	130ppm (for 1h)	65%	200°C
Lab-Ce-02	157ppm (for 1h)	78.5%	200°C

Table 2: Data on Effectiveness of Catalysts on Removal of NO₂

Referring to Figure 7 and Figure 8, bar charts illustrating the average percentage of NO/NO₂ removed by catalyst, Lab-Ce-01, at 50-minutes intervals are provided. It was observed that

high temperature was found to enhance the removal of NO and NO₂ at the catalyst bed but it could cause sintering of catalyst leading to poor performance of catalyst as the experiment progresses in the reactor. The optimum temperature is 150°C.

- 5 The catalysts may be regenerated by introducing oxygen gas into the catalyst bed. The oxygen gas may be introduced at a predetermined temperature and flow rate. The temperature is preferably between 120°C to 200°C. The flow rate of the flue gas is preferably 25L/h. The flow rate of the flue gas may also be from 25L/h or at least 25L/h.
- 10 In summary, Table 3 shows the experimental parameters for the testing of catalysts in the reactor.

Parameter	Description
Type of Catalyst to be tested	- Commercial CeO₂ - Lab-Ce-01 - Lab-Ce-02 - Lab-Ce-03 - Lab-Ce-doped-01 - Lab-Ce-doped-02 - Lab-Ce-doped-03 - Lab-Ce-doped-04 - Lab-Ce-doped-05 - Lab-Ce-doped-06 - Lab-Ce-doped-07
Type of Flue Gas	200ppm NO 200ppm NO₂ <u>Note 01:</u> The flue gases used in the tests were pre-blended with argon.
Mesh Size	106um and 75um <u>Note 02:</u> Catalyst powders were sieved through different mesh numbers before they were tested in the SCR.
Temperature in catalytic bed	120°C 130°C 140°C 150°C 160°C 200°C
Flow of Gas	25L/h
Duration of each Test in SCR	4h

Table 3: Parameters used in testing of different catalysts in the reactor

- 5 Whilst there has been described in the foregoing description preferred embodiments of the present invention, it will be understood by those skilled in the technology concerned that many variations or modifications in details of design or construction may be made without departing from the present invention.

Claims

1. A method for reducing the amount of NO_x in a flue gas, the method comprising:
 - (a) reacting the NO_x with a catalyst at a temperature between 120°C to 200°C;
5 and
 - (b) discharging the flue gas containing a reduced amount of NO_x to the atmosphere;
wherein the catalyst is contained within a fluidised bed reactor.
- 10 2. The method according to claim 1, further comprising precipitating the catalyst prior reacting it with the NO_x in the flue gas.
3. The method according to any one of claims 1 or 2, wherein the catalyst is a rare earth metal oxide.
- 15 4. The method according to any one of claim 3, wherein the catalyst is cerium dioxide.
5. The method according to claim 4, wherein the catalyst is prepared by mixing a cerium salt and an alkali.
- 20 6. The method according to claim 5, wherein the cerium salt is cerium nitrate and the alkali is any alkali selected from the group consisting of: sodium hydroxide, hexamethylenetetramine and ammonium hydroxide.
- 25 7. The method according to any one of claims 4 to 6, wherein the cerium dioxide is doped with 0.5mol% to 20mol% copper oxide and/or zirconium dioxide based on the weight of cerium dioxide.
8. The method according to any one of the preceding claims, wherein the catalyst is
30 present in powder form.
9. The method according to claim 8, wherein the particle size of the catalyst is between 5.5nm to 30nm.
- 35 10. The method according to any one of the preceding claims, wherein the flue gas is introduced into the reactor at a flow rate from 25L/h.

11. The method according to any one of the preceding claims, wherein the concentration of NO_x in the flue gas is 200ppm.

12. The method according to any one of the preceding claims, further comprising
5 reacting the NO_x with the catalyst in the presence of a balance gas.

13. The method according to claim 12, wherein the balance gas is argon.

14. The method according to claim 13, wherein the concentration of argon present in the
10 flue gas is 200ppm.

15. The method according to any one of the preceding claims, wherein the 83% of the NO_x in the flue gas is removed.