

[54] METHODS FOR CATALYTIC REDUCTION OF NITROGEN OXIDES

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Primary Examiner—G. O. Peters

[57] ABSTRACT

Process for removing nitrogen oxides from gaseous mixtures comprising the same. Ammonia in an amount excessive over the stoichiometric amount necessary for reducing the nitrogen oxides is introduced into a reaction zone containing a catalyst. Then, ammonia in a minimum amount necessary for reduction of the nitrogen oxides is introduced into the reaction zone.

11 Claims, 1 Drawing Figure



## METHODS FOR CATALYTIC REDUCTION OF NITROGEN OXIDES

### BACKGROUND OF THE INVENTION

This invention relates to a process for reducing the concentration of nitrogen oxides contained in a gaseous mixture. In particular, this invention relates to a process wherein the concentration of nitrogen oxides is reduced by catalytic reduction.

Nitrogen oxides are, of course, generally present in significant quantities in gaseous mixtures such as flue gases. Different methods have been used in the treatment of these gas mixtures. One type of treatment involves the catalytic reduction of the nitrogen oxides. As processes for catalytic reduction, two methods are known in the art: (1) a non-selective reduction method in which carbon monoxide, hydrogen or a lower hydrocarbon is used as the reducing agent, and (2) a selective reduction method in which ammonia is used as the reducing agent. The latter catalytic reduction method (using ammonia) is advantageous in that the amount of the reducing agent used can be reduced and nitrogen oxides can be removed at a high ratio. Accordingly, various modifications and improvements have been proposed on this method.

These reduction methods using ammonia are roughly classified into two groups, namely one in which a noble metal component such as platinum, palladium, rhodium, or iridium is used as the catalyst and another in which a base metal, particularly a non-noble transition metal component such as copper, iron, vanadium, chromium or molybdenum is used as the catalyst.

Noble metal catalysts are defective in that they are drastically poisoned by sulfur oxides generally contained in exhaust gases, and base metal catalysts are defective in that severe reaction conditions such as elevated reaction temperatures and reduced space velocities should be adopted in order to improve their activities. In view of the fact that exhaust gases discharged in large quantities from boilers which have now a very large scale should be treated for removal of nitrogen oxides therefrom and temperatures of these exhaust gases are generally low, it is desirable to develop a method in which nitrogen oxides can be removed effectively under such reaction conditions as a lower temperature and a higher space velocity. Further, if ammonia added as the reducing agent is discharged into open air in the unreacted state, there is a fear that it causes another environmental pollution. Accordingly, it is also desirable to develop a method in which no unreacted ammonia is discharged.

### SUMMARY OF THE INVENTION

In accordance with this invention, gaseous mixtures such as flue gases are treated to reduce the nitrogen oxides content thereof by contacting with a catalyst an amount of ammonia in excess of the stoichiometric amount necessary to reduce the nitrogen oxides in the gaseous mixture. Next, the gaseous mixture is contacted with a zeolite catalyst in the presence of the minimum amount of ammonia necessary to reduce the nitrogen oxides contained therein.

### BRIEF DESCRIPTION OF THE DRAWING

The Figure is a graph depicting the performance of the method of the present invention compared to prior art methods.

## DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, nitrogen oxides are removed from a gas containing the nitrogen oxides and oxygen by contacting the resulting gaseous mixture with a catalyst in the presence of ammonia to reduce the nitrogen oxides selectively.

In short, the present invention relates to a method for selectively reducing nitrogen oxides contained in exhaust gases from stationary sources, such as flue gas from the combustion furnace of power plants, by using ammonia as a reducing agent, and the most characteristic feature of the present invention resides in that the catalyst used is contacted with ammonia in an amount excessive over the stoichiometric amount necessary for reduction of nitrogen oxides in an exhaust gas to thereby activate the catalyst and then, the amount of ammonia is reduced to a minimum amount necessary for reduction of the nitrogen oxides to thereby effect the catalytic reduction.

A typical instance of a nitrogen oxide-containing exhaust gas to which the method of the present invention is applied is an exhaust gas from a fixed combustion apparatus using coal or petroleum as a fuel, and this exhaust gas has, in general, the following composition:

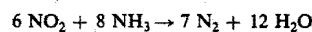
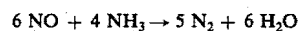
NO<sub>x</sub>: about 100 to about 1,000 ppm  
 SO<sub>x</sub>: about 100 to about 3,000 ppm  
 O<sub>2</sub>: about 1 to about 10%  
 CO<sub>2</sub>: about 7 to about 13%  
 steam: about 7 to about 13%

As pointed out hereinabove, a flue exhaust gas generally contains a sulfur oxides and oxygen in addition to nitrogen oxides. Accordingly, it is necessary to perform removal of nitrogen oxides while eliminating influences of sulfur oxides and oxygen. The nitrogen oxide present in flue gas (hereinafter referred to as "NO<sub>x</sub>") is composed mainly of nitrogen monoxide (NO) and nitrogen dioxide (NO<sub>2</sub>). The nitrogen oxide content in the flue gas depends on combustion conditions such as the nitrogen compound content in a fuel, the amount of air and the combustion temperature. The sulfur oxide content in the flue gas varies depending on the sulfur compound content in the fuel.

Ammonia is contacted with the exhaust gas maintained at about 200° to about 500° C. For example, in the case of an exhaust gas from a combustion furnace of a power plant, ammonia is added to the exhaust gas maintained at about 200° to about 500° C., which has been passed through an economizer.

In the activating treatment of the present invention, ammonia is contacted with the exhaust gas in an amount excessive over the stoichiometric amount necessary for reduction of nitrogen oxides contained in the exhaust gas.

Reduction of nitrogen oxides to nitrogen is expressed by the following reaction formulae:



In the catalyst activating treatment of the present invention, the amount of ammonia is so selected that unreacted ammonia is not discharged, and it is generally at least about 1.2 times the stoichiometric amount. It is

preferred that ammonia be introduced in an amount about 1.2 to about 3 times the stoichiometric amount.

This activating treatment is characterized in that the above-mentioned excessive amount of ammonia is added at prescribed intervals while the reduction reaction of nitrogen oxides is being performed. It is also possible to accomplish this activating treatment by mixing ammonia into nitrogen or air before the start of reduction of nitrogen oxides and contacting the catalyst with the resulting gaseous mixture. It is preferred that this activating treatment be conducted under the same conditions as adopted for the reduction reaction of nitrogen oxides.

After completion of this activating treatment, the amount of ammonia introduced in the reaction zone is adjusted to a minimum amount necessary for reduction of nitrogen oxides, generally not larger than about 1.2 times the stoichiometric amount, especially about 1.0 to about 0.7 times the stoichiometric amount.

It is preferred that contact of the nitrogen oxide-containing exhaust gas with the catalyst be performed by passing the exhaust gas through a fixed bed of the catalyst. As the reaction conditions, there may be adopted a reaction temperature of about 200° to about 500° C., preferably about 250° to about 400° C., and a gas space velocity of about 2,000 to about 100,000 V/H/V, preferably about 5,000 to about 30,000 V/H/V. Since the activity of the ammonia reduction of nitrogen oxides is lowered at higher or lower temperatures, good results are obtained when a mixture of the exhaust gas and ammonia is contacted with the catalyst bed at a temperature within the above-mentioned range.

As the catalyst that can be used for practicing the method of the present invention, there can be mentioned (1) a crystalline aluminosilicate, (2) a product obtained by exchanging an alkali metal ion in a crystalline aluminosilicate with at least one metal cation having an activity of reducing nitrogen oxides, and (3) a supported catalyst formed by supporting, by the impregnation treatment, an active metal component capable of reducing nitrogen oxides on a carrier obtained by removing an alkali metal ion from a crystalline aluminosilicate.

The above-mentioned crystalline aluminosilicates used in the present invention have a chain, laminate or three-dimensional reticulate framework structure wherein methane-type SiO<sub>4</sub> tetrahedra are combined with AlO<sub>4</sub> tetrahedra through oxygen atoms. The AlO<sub>4</sub> tetrahedra have a negative charge and, therefore, combine with a corresponding cation. The water of crystallization is thereby kept by the electrostatic force of the cation. The cations generally include alkali metal ions and alkaline earth metal ions.

Spaces surrounded by the reticulate structures of SiO<sub>4</sub> tetrahedra and AlO<sub>4</sub> tetrahedra form cavities or paths comprising the cavities connected with each other. Water of crystallization is kept in the cavities. By heating, the water is removed to leave porous adsorption medium.

Substances to be adsorbed are introduced in the cavities or paths through pores of the reticulate structure and thereby adsorbed therein. The pores having a uniform diameter exhibit a molecular sieve effect; namely, only molecules having diameters smaller than pore diameter are adsorbed and thereby separated, leaving molecules of larger diameters.

The crystalline aluminosilicates are classified according to pore diameter and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio. In the

present invention, those having pore diameters in the range of about 3-15 Å and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of above about 2 are preferred. As the crystalline aluminosilicate, there may be used both natural and synthetic zeolites.

Suitable natural zeolites are:

- Mordenite: (Ca, K<sub>2</sub>, Na<sub>2</sub>) [AlSi<sub>3</sub>O<sub>12</sub>]<sub>2</sub> · 7H<sub>2</sub>O
- Erionite: (K<sub>2</sub>, Na<sub>2</sub>, Ca) [AlSi<sub>3</sub>O<sub>8</sub>]<sub>2</sub> · 6H<sub>2</sub>O
- Natrolite: Na<sub>2</sub>[Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>] · 2H<sub>2</sub>O
- Chabazite: (Ca, Na<sub>2</sub>) [Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>] · 6H<sub>2</sub>O
- Faujasite: Na<sub>2</sub>Ca [Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>]<sub>2</sub> · 16H<sub>2</sub>O

The natural zeolites contain alkaline earth metals, with alkali metals.

As the synthetic zeolites, there may be used synthetic faujasite and synthetic mordenite. The synthetic faujasites include:

- Zeolite-A: 1.0 ± 0.2M<sub>2/n</sub>O : Al<sub>2</sub>O<sub>3</sub> : 1.85 ± 0.5SiO<sub>2</sub> : YH<sub>2</sub>O (wherein M represents a metal, n represents a valence of M and Y represents a number of about 6 or below).
- Zeolite-X: 1.0 ± 2M<sub>2/n</sub>O : Al<sub>2</sub>O<sub>3</sub> : 5 ± 0.5SiO<sub>2</sub> : YH<sub>2</sub>O (wherein M represents a metal of a valence of from 1 to 3, inclusive, n represents a valence of M and Y represents a number of about 8 or below).
- Zeolite-Y: 0.9 ± 0.2Na<sub>2</sub>O : Al<sub>2</sub>O<sub>3</sub> : WSiO<sub>2</sub> : YH<sub>2</sub>O (wherein W represents a number between 3 and 6, inclusive, and Y represents a number of about 9 or below).

The synthetic mordenites include, for example:

- Zeolite-L: 1.0 ± 0.1M<sub>2/n</sub>O : Al<sub>2</sub>O<sub>3</sub> : 0.4 ± 0.5SiO<sub>2</sub> : YH<sub>2</sub>O (wherein M represents a metal, n represents a valence of M, and Y represents a number from 0 to 7, inclusive).

Especially preferred crystalline aluminosilicates are those having a pore diameter in the range of about 6-13 Å and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of about 2-6. For example, synthetic faujasite having a pore diameter of about 8-9 Å and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of about 2-3 and other synthetic faujasites having a pore diameter of about 8-9 Å and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of about 4-6 are preferred.

A zeolite catalyst having incorporated therein an active metal ion is prepared by contacting a crystalline aluminosilicate with an aqueous or organic solution of an active metal compound according to a customary method. The ion exchange ratio is not particularly critical, but it is generally preferred that the ion exchange ratio be about 60 to about 100%.

As the active metal, there is employed at least one member selected from copper, cobalt, nickel, vanadium, molybdenum, chromium, tungsten, manganese, platinum, silver and iridium.

The catalyst suitable for the practice of the present invention is formed by reducing the content of alkali metal in a crystalline aluminosilicate below 0.6 equivalent per gram atom of aluminum and supporting at least one active metal compound on the so treated aluminosilicate by the impregnation treatment.

The ion-exchange for reducing the alkali metal content in the aluminosilicate below 0.6 equivalent per gram atom of aluminum may be accomplished by any method, as far as it can reduce the alkali metal content below the above-mentioned level. In general, this ion exchange is accomplished by contacting an aluminosilicate with an aqueous or non-aqueous (organic solvent or the like) solution containing a hydrogen ion, an ion



capable of being converted to a hydrogen ion, an alkaline earth metal ion or a rare earth metal ion. For this ion exchange treatment, water is the medium most preferred in view of the operation and apparatus. Any organic solvents capable of ionizing the metal compound used can also be employed. For example, alcohols such as methanol, ethanol, propanol and butanol, amides such as dimethylformamide and diacetamide, ethers and ketones are preferably employed.

An ion convertible into hydrogen ion is ammonium ion from organic and inorganic ammonium compounds such as ammonium chloride, ammonium sulfate, ammonium carbonate, ammonium bromide, ammonium bicarbonate, ammonium sulfide, ammonium nitrate, ammonium formate, ammonium acetate, ammonium hydroxide, tetraalkyl ammonium (tetramethyl ammonium) and tetramethyl ammonium hydroxide. The aluminosilicates ion-exchanged with ammonium ion are converted into hydrogen ion-containing aluminosilicates by calcination, thereby releasing ammonia.

As rare earth metal ion sources, there may be used salts of metals such as cerium, lanthanum and praseodymium. Suitable salts include, for example, chlorides, sulfates, sulfides, nitrates, nitrites, carbonates, bicarbonates, acetates, benzoates, formates and tartarates. Particularly preferred metal salts are chlorides, nitrates and acetates.

As alkaline earth metal ion sources, there may be used inorganic and organic salts such as chlorides, bromides, carbonates, sulfates, nitrates, acetates, formates, oxalates of calcium, magnesium and strontium.

The ion exchange treatment for the catalyst will now be described.

An alkali metal-containing aluminosilicate is immersed once or repeatedly in a medium containing a hydrogen ion, an ion capable of being converted to a hydrogen ion, an alkaline earth metal ion or a rare earth metal ion. Alternatively, a medium containing a cation such as mentioned above is conveyed through a contact column packed with an alkali metal-containing aluminosilicate to bring the aluminosilicate into contact with such medium. The specific amount of the alkali metal is removed from the aluminosilicate by the ion exchange with the above-mentioned cation.

Such conditions as the cation concentration in the medium, the contact time and the amount of the aluminosilicate used for the ion exchange are chosen so that the the alkali metal content in the aluminosilicate is reduced below 0.6 equivalent, preferably 0.2 to 0.6 equivalent per gram atom of aluminum.

The aluminosilicate ion-exchanged with ammonia can be converted to a hydrogen ion-exchanged aluminosilicate by washing the aluminosilicate and calcining it at about 300° to about 700° C. to release the ammonium ion.

An especially preferred ion-exchange method is one in which the alkali metal ion is exchanged with an ammonium ion.

In addition to the crystalline aluminosilicate, there may be employed a mixture of crystalline aluminosilicate and, incorporated therein, about 1 to about 30% by weight of a refractory substance. Examples of refractory substances include at least one inorganic oxide selected from alumina, magnesia, titania, zirconia, hafnia, silica and diatomaceous earth. Further, in preparing a molded article of the catalyst, it is possible to add a suitable amount, for example, about 2 to about 40% by weight, of alumina sol or the like as a binder.

The above-mentioned active metal component having an activity of reducing nitrogen oxides is supported on the thus prepared aluminosilicate carrier by the impregnation treatment. Most preferred metals are copper, iron, chromium, and vanadium, and better results are obtained when at least one metal selected from them is employed.

The active metal component is preferably employed in the form of a metal, a metal oxide, a metal sulfate or a mixture thereof. An especially preferred form is a sulfate in the case of copper and iron and an oxide in the case of chromium and vanadium.

The amount of the active metal component in the catalyst is a catalytically effective amount, for example, about 1 to about 20% by weight (as metal), preferably about 2 to about 10% by weight, based on the final catalyst.

The active metal component is supported on the aluminosilicate by the impregnation treatment. This impregnation treatment comprises steps of immersing the above-mentioned aluminosilicate carrier in an impregnation solution formed by dissolving a soluble compound of the active metal in a suitable medium and separating from the solution the active metal component-impregnated carrier. The concentration of the active metal compound in the impregnation solution, the amount of the solution is used for the impregnation treatment, the impregnation time and the impregnation temperature are chosen appropriately so that a desired amount of the active metal component is supported on the aluminosilicate carrier.

The preferred impregnation time is about 5 minutes to about 1 hour, which is much shorter than the time required in the ion exchange method. It is important that the active metal component should be supported under such conditions that cations in the aluminosilicate, such as alkali metal, alkaline earth metal, hydrogen and rare earth metal ions, are not removed from the aluminosilicate.

The soluble compound of the active metal to be used for the impregnation treatment is a compound that can be decomposed at a high temperature and can be converted to an oxide by calcination. Preferred soluble compounds include inorganic salts such as nitrates, chlorides and sulfates and organic salts such as acetates, tartarates and oxalates.

As the medium of the impregnation solution, there may be employed water, inorganic acids, organic acids, other organic solvents and mixtures thereof. Preferred inorganic acids are hydrochloric acid, nitric acid and sulfuric acid. Preferred organic acids are mono- and poly-carboxylic acids such as acetic acid and citric acid.

As other organic solvent, there are preferably employed alcohols, aldehydes, amines and esters. Alcohols having 1 to 10 carbon atoms, especially isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, pentyl alcohol and isopentyl alcohol, are preferably employed. Aldehydes having 1 to 10 carbon atoms, especially acetaldehyde, ethylaldehyde and propylaldehyde, are preferably employed. As the amine, there can be employed, for example, alkyl amines such as dimethyl amine and triethyl amine, and as the ester, there can be used, for example, ethyl formate, ethyl acetate, isopropyl acetate and butyl acetate.

Impregnation of the active metal component will now be described by reference to copper as the active metal component.

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