

[54] METHOD FOR REDUCTION OF NITROGEN OXIDES WITH AMMONIA USING PROMOTED ZEOLITE CATALYSTS

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[52] U.S. Cl. 423/239

[58] Field of Search 423/239 A, 239, 235, 423/235 D

[56] References Cited

U.S. PATENT DOCUMENTS

3,895,094	7/1975	Carter et al.	423/239
4,104,361	8/1978	Nishikawa et al.	423/239
4,220,632	9/1980	Pence et al.	423/239
4,473,535	9/1984	Kittrell et al.	423/239
4,735,927	4/1988	Gerdes et al.	423/239

Primary Examiner—Gregory A. Heller

[57] ABSTRACT

A method in accordance with the invention comprises

passing through a zeolite catalyst as described below, a gaseous stream containing nitrogen oxides, ammonia and oxygen to selectively catalyze the reduction of nitrogen oxides and, if excess or unreacted ammonia is present, to oxidize the excess of unreacted ammonia with oxygen to hydrogen and water. The method includes the use of a zeolite catalyst composition which comprises a metal (e.g., iron or copper) promoted zeolite, the zeolite being characterized by having a silica to alumina ratio of at least about 10 and a pore structure which is interconnected in all three crystallographic dimensions by pores having an average kinetic pore diameter of at least about 7 Angstroms. Promoted zeolites of the above type have demonstrated high tolerance for sulfur poisoning, good activity for the selective catalytic reduction of nitrogen oxides with ammonia, good activity for the oxidation of ammonia with oxygen, and the retention of such good activities even under high temperature operations, e.g., 400° C. or higher, and hydrothermal conditions.

7 Claims, 2 Drawing Sheets

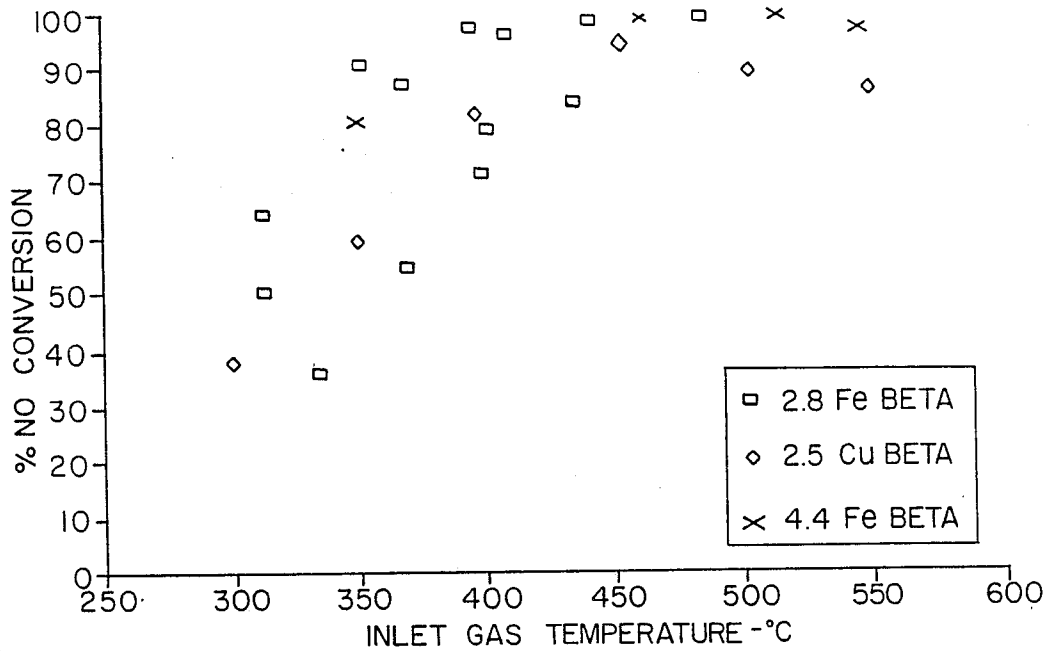


FIG. 1

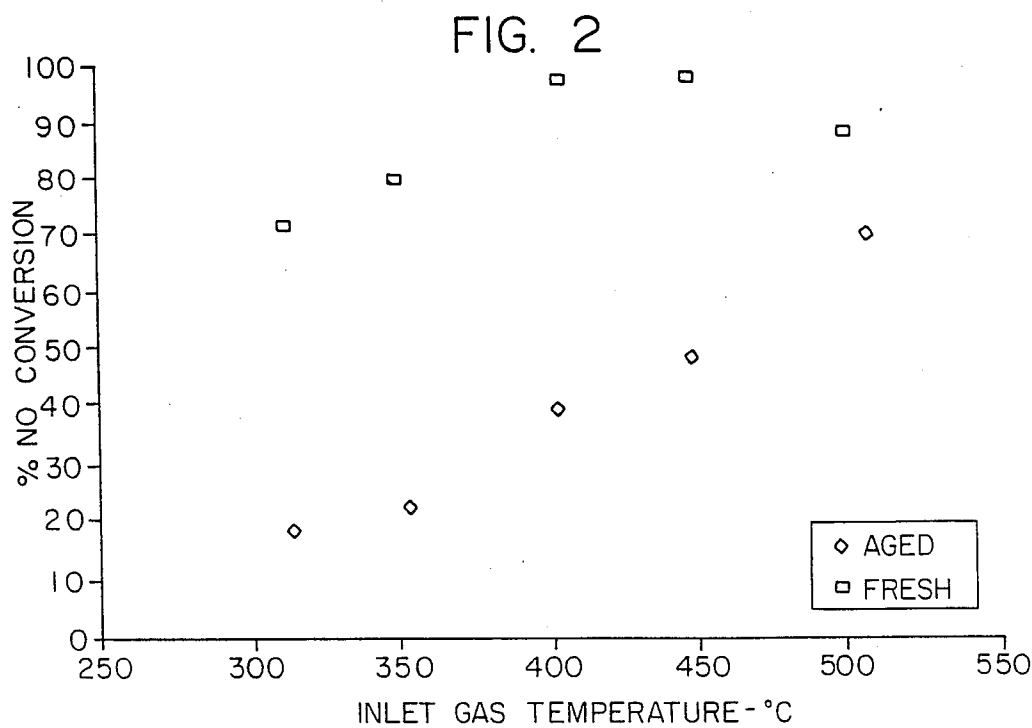


FIG. 2

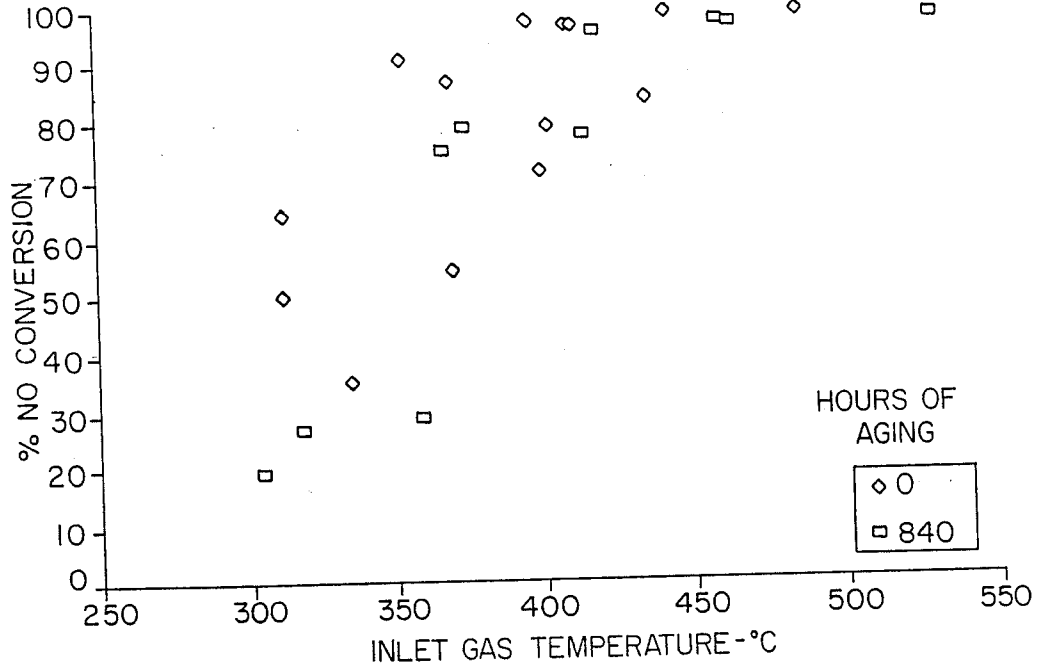
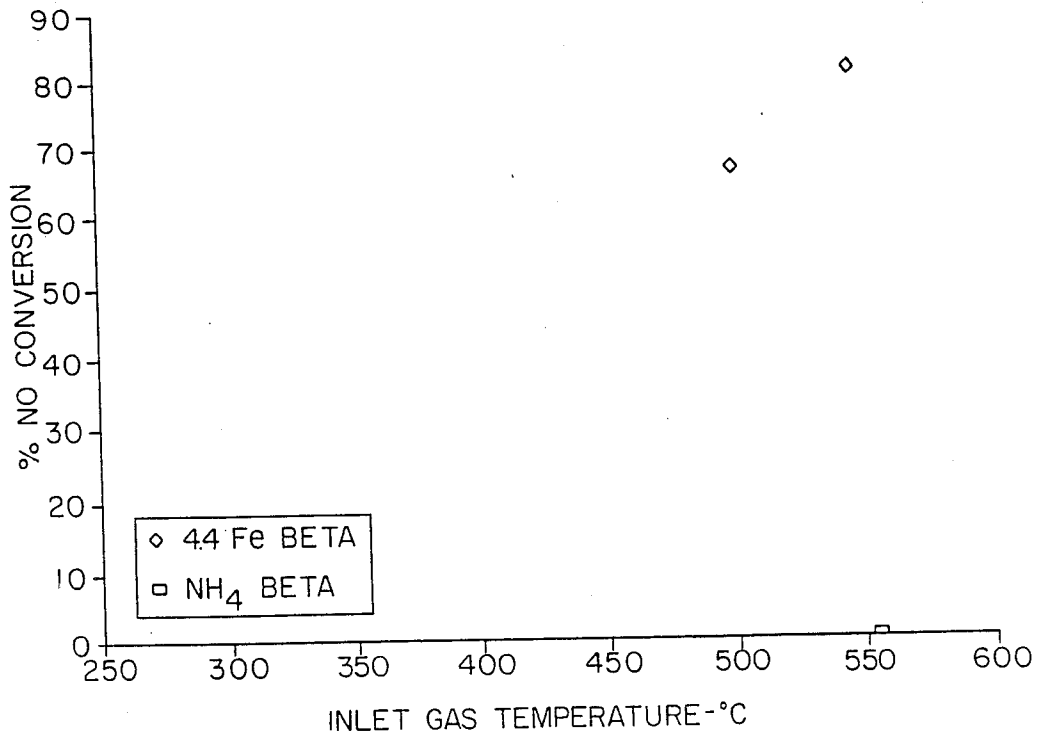


FIG. 3

FIG. 4



METHOD FOR REDUCTION OF NITROGEN OXIDES WITH AMMONIA USING PROMOTED ZEOLITE CATALYSTS

BACKGROUND OF THE INVENTION

1. Field of The Invention

The present invention is concerned with a method of catalyzing the reduction of nitrogen oxides with ammonia, especially the selective reduction of nitrogen oxides with ammonia in the presence of oxygen, using zeolite catalysts, especially metalpromoted zeolite catalysts.

2. The Related Art

Both synthetic and natural zeolites and their use in promoting certain reactions, including the selective reduction of nitrogen oxides with ammonia in the presence of oxygen, are well known in the art. Zeolites are aluminosilicate crystalline materials having rather uniform pore sizes which, depending upon the type of zeolite and the type and amount of cations included in the zeolite lattice, range from about 3 to 10 Angstroms in diameter.

Japanese Patent Publication (Kokai) No. 51-69476, published Jun. 16, 1976 on Application No. 49-142463, filed Dec. 13, 1974, discloses a method for reducing nitrogen oxides in waste gases by reaction with ammonia in the presence of a metal-promoted, dealuminized synthetic or natural mordenite zeolite. The resistance of the catalyst to sulfurous poisons, particularly sulfur trioxide and sulfuric acid mist, is said to be enhanced by dealuminizing the mordenite to increase the silica to alumina ratio to more than 12, preferably to more than 15. The zeolite is promoted with 0.5 to 30 weight percent of at least one of a number of promoters including copper, vanadium, chromium, iron, cobalt or nickel and used at a reaction temperature of 200° to 500° C. with from 0.5 to three times the stoichiometric amount of ammonia reductant. Example 1 of the Publication illustrates an iron-promoted mordenite ore as being effective for the reduction of nitrogen oxides. In connection with Example 2, it is stated that a slight decrease of the activity of a high silica to alumina ratio, copper-promoted mordenite catalyst is recognized when sulfur trioxide is included in the gas stream. However, an "extreme improvement" of resistance to sulfur trioxide poisoning is noted in comparison with a copper mordenite which has not been dealuminized to increase the silica to alumina ratio.

UK patent application No. 2,193,655A discloses a catalyst containing a low surface area titania and a copper-promoted zeolite for use in the reduction of nitrogen oxides with ammonia. The zeolite has an average pore diameter of 10 Angstroms or less, preferably 8 Angstroms or less, and a silica to alumina molar ratio of 10 or more, preferably 20 or more; the resultant titania-promoted zeolite catalysts having these characteristics are stated to have good mechanical strength and to be resistant to volatile catalyst poisons such as arsenic, selenium, tellurium, etc., contained in exhaust gases. Examples of suitable zeolites are mordenite, ZSM-5, and ferrierite.

U.S. Pat. No. 4,297,328 discloses a "three-way conversion" catalytic process for the simultaneous catalytic oxidation of carbon monoxide and hydrocarbons and reduction of nitrogen oxides for purifying the exhaust gas of automobile engines operated within a prescribed range of air to fuel ratio (column 4, lines 63-68). The disclosed catalyst is a copper-promoted zeolite having a

silica to alumina ratio greater than 10, preferably greater than 20 (column 6, lines 23-28). Representative high-silica zeolites are described at columns 6-8 of the patent and include (column 6, lines 29-33) silicalite (as described in U.S. Pat. No. 4,061,724), ZSM-5, ZSM-8, ZSM-11, ZSM-12, hyper Y, ultrastabilized Y, Beta, mordenite and erionite. Ultrastabilized Y is described (column 7, lines 22-25) as "a form of zeolite Y which has been treated to give it the organophilic characteristic of the adsorbents of the present invention." Example 6 of the patent is stated to show no measureable loss in combustion activity of the copper-promoted zeolite catalyst due to sulfur poisoning (exposure of the catalyst to methylmercaptan in the gaseous stream). The patent thus discloses the utility of the copper-promoted specified zeolites for three-way conversion in an exhaust gas generated by a lean air to fuel ratio combustion mixture.

The art thus shows an awareness of the utility of metal-promoted zeolite catalysts including, among others, iron-promoted and copper-promoted zeolite catalysts, for the selective catalytic reduction of nitrogen oxides with ammonia.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a method for the reduction of nitrogen oxides with ammonia, the method comprising the following steps. A gaseous stream containing nitrogen oxides and ammonia, and which may also contain oxygen, is contacted at a temperature of from about 250° C. to 600° C. with a sulfur-tolerant catalyst composition. The catalyst composition comprises a zeolite having a silica to alumina ratio of at least about 10, and a pore structure which is interconnected in all three crystallographic dimensions by pores having an average kinetic pore diameter of a least about 7 Angstroms, e.g., from about 7 to 8 Angstroms, and one or both of an iron and a copper promoter present in the zeolite, for example, in the amount of from about 0.1 to 30 percent by weight, preferably from about 1 to 5 percent by weight, of the total weight of promoter plus zeolite.

Another aspect of the invention provides that the promoter is an iron promoter.

Still another aspect of the present invention provides that the zeolite comprises one or more of USY, Beta and ZSM-20. A refractory binder may be admixed with the zeolites.

The gaseous stream may contain from about 0.7 to 2 moles of ammonia per mole of nitrogen oxides. Oxygen may also be present in the gaseous stream in an amount of from about 0.5 to 30 volume percent of the gaseous stream.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot showing the percent conversion of NO versus inlet temperature for various metal-promoted zeolite catalysts;

FIG. 2 is a plot showing the percent conversion of NO versus the inlet temperature of a gaseous stream to be treated for aged and fresh copper-promoted zeolite catalysts;

FIG. 3 is a plot showing the percent conversion of NO versus inlet temperature of a gas stream passed through aged and fresh iron promoted beta zeolite catalysts; and

FIG. 4 is a plot showing the percent conversion of ammonia versus inlet temperature of a gas stream fed to different beta zeolite catalysts.

References herein and in the claims to a zeolite catalyst containing a percent "by weight" promoter means a percentage calculated as the weight of promoter, as the metal, divided by the combined weights of promoter (as the metal) plus the zeolite.

Reference herein and in the claims to "metal", "iron" and "copper" with respect to the promoters should not be taken to imply that the promoter is necessarily in the elemental or zero valence state; the terms enclosed in quotes should be understood to include the presence of promoters as they exist in the catalyst compositions, e.g., as exchanged ions and/or impregnated ionic or other species.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS THEREOF

In order to reduce the emissions of nitrogen oxides from flue and exhaust gases, such as the exhaust generated by gas turbine engines, ammonia is added to the gaseous stream containing the nitrogen oxides and the gaseous stream is then contacted with a suitable catalyst at elevated temperatures in order to catalyze the reduction of nitrogen oxides with ammonia. Such gaseous streams often inherently contain substantial amounts of oxygen. For example, a typical exhaust gas of a turbine engine contains from about 2 to 15 volume percent oxygen and from about 20 to 500 volume parts per million nitrogen oxides, the latter normally comprising a mixture of NO and NO₂. Usually, there is sufficient oxygen present in the gaseous stream to oxidize residual ammonia, even when an excess over the stoichiometric amount of ammonia required to reduce all the nitrogen oxides present is employed. However, in cases where a very large excess over the stoichiometric amount of ammonia is utilized, or wherein the gaseous stream to be treated is lacking or low in oxygen content, an oxygen-containing gas, usually air, may be introduced between the first catalyst zone and the second catalyst zone, in order to insure that adequate oxygen is present in the second catalyst zone for the oxidation of residual or excess ammonia. The reduction of ammonia with nitrogen oxides to form nitrogen and H₂O can be catalyzed by metal-promoted zeolites to take place preferentially to the oxidation of ammonia by the oxygen, hence the process is often referred to as the "selective" catalytic reduction ("SCR") of nitrogen oxides, and is sometimes referred to herein simply as the "SCR" process.

The catalysts employed in the SCR process ideally should be able to retain good catalytic activity under high temperature conditions of use, for example, 400° C. or higher, under hydrothermal conditions and in the presence of sulfur compounds. High temperature and hydrothermal conditions are often encountered in practice, such as in the treatment of gas turbine engine exhausts. The presence of sulfur or sulfur compounds is often encountered in treating the exhaust gases of coal-fired power plants and of turbines or other engines fueled with sulfurcontaining fuels such as fuel oils and the like.

Theoretically, it would be desirable in the SCR process to provide ammonia in excess of the stoichiometric amount required to react completely with the nitrogen oxides present, both to favor driving the reaction to completion and to help overcome inadequate mixing of

the ammonia in the gaseous stream. However, in practice, significant excess ammonia over the stoichiometric amount is normally not provided because the discharge of unreacted ammonia from the catalyst would itself engender an air pollution problem. Such discharge of unreacted ammonia can occur even in cases where ammonia is present only in a stoichiometric or sub-stoichiometric amount, as a result of incomplete reaction and/or poor mixing of the ammonia in the gaseous stream. Channels of high ammonia concentration are formed in the gaseous stream by poor mixing and are of particular concern when utilizing catalysts comprising monolithic honeycomb-type carriers comprising refractory bodies having a plurality of fine, parallel gas flow paths extending therethrough because, unlike the case with beds of particulate catalysts, there is no opportunity for gas mixing between channels. It is therefore also desirable that the catalyst employed to catalyze the selective catalytic reduction of nitrogen oxides, be effective to catalyze the reaction of oxygen and ammonia, in order to oxidize excess or unreacted ammonia to N₂ and H₂O.

The present invention is predicated on the discovery that a certain class of zeolites, especially when promoted with a promoter such as iron or copper, especially iron, exhibits desired characteristics as described above by providing a sulfur tolerant catalyst which shows good activity for both (1) the selective catalytic reduction of nitrogen oxides by reaction with ammonia, even in the presence of oxygen, and (2) the oxidation of ammonia with oxygen when nitrogen oxides are at very low concentrations. The catalysts of the present invention retain such activity even after prolonged exposure to high temperatures, hydrothermal conditions, and sulfate contamination of the type often encountered in use, e.g., in the treatment of coal-fired power plants or turbine engine exhaust gases.

Generally, in accordance with the practices of the present invention, a catalyst is provided which comprises a zeolite having specific properties as described below, and which is promoted by a metal, preferably iron, in order to enhance its catalytic activity. The zeolite may be provided in the form of a fine powder which is admixed with or coated by a suitable refractory binder, such as bentonite or silica, and formed into a slurry which is deposited upon a suitable refractory carrier. Typically, the carrier comprises a member, often referred to as a "honeycomb" carrier, comprising one or more refractory bodies having a plurality of fine, parallel gas flow passages extending therethrough. Such carriers are, of course, well known in the art and may be made of any suitable material such as cordierite or the like. The catalysts of the present invention may also be provided in the form of extrudates, pellets, tablets or particles of any other suitable shape, for use as a packed bed of particulate catalyst, or as shaped pieces such as plates, saddles, tubes or the like.

The catalysts of the present invention show a marked resistance to poisoning by sulfates (or other sulfur compounds) which are often contained in the gas streams which are treatable by the catalysts of the present invention. Without wishing to be bound by any particular theory, it appears that SO₂ poisoning has both short term and long term effects. For example, flowing a gas stream containing 2,000 parts per million by volume ("Vppm") SO₂ through catalysts comprising copper-promoted small to medium pore zeolites such as ZSM-5, naturally occurring chabazite and clinoptilolite, resulted in 10 to 40 percent reduction in SCR process

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