

United States Patent [19]

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Speronello et al.

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[54] **STAGED METAL-PROMOTED ZEOLITE CATALYSTS AND METHOD FOR CATALYTIC REDUCTION OF NITROGEN OXIDES USING THE SAME**

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[73] Assignee: **Engelhard Corporation**, Iselin, N.J.

[21] Appl. No.: **678,777**

[22] Filed: **Apr. 1, 1991**

Related U.S. Application Data

[62] Division of Ser. No. 340,992, Apr. 20, 1989, Pat. No. 5,024,981.

[51] Int. Cl.⁶ **B01D 53/56; B01D 53/58**

[52] U.S. Cl. **423/235; 423/237; 423/239.2**

[58] Field of Search **423/213.2, 213.5, 423/213.7, 235, 237, 239, 246, 239.2; 502/43**

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,970,739	7/1976	Shiraishi et al.	423/235 S
4,297,328	10/1981	Ritscher et al.	423/213.2
4,961,917	10/1990	Byrne	423/239
5,041,270	8/1991	Fujitani et al.	423/213.2

FOREIGN PATENT DOCUMENTS

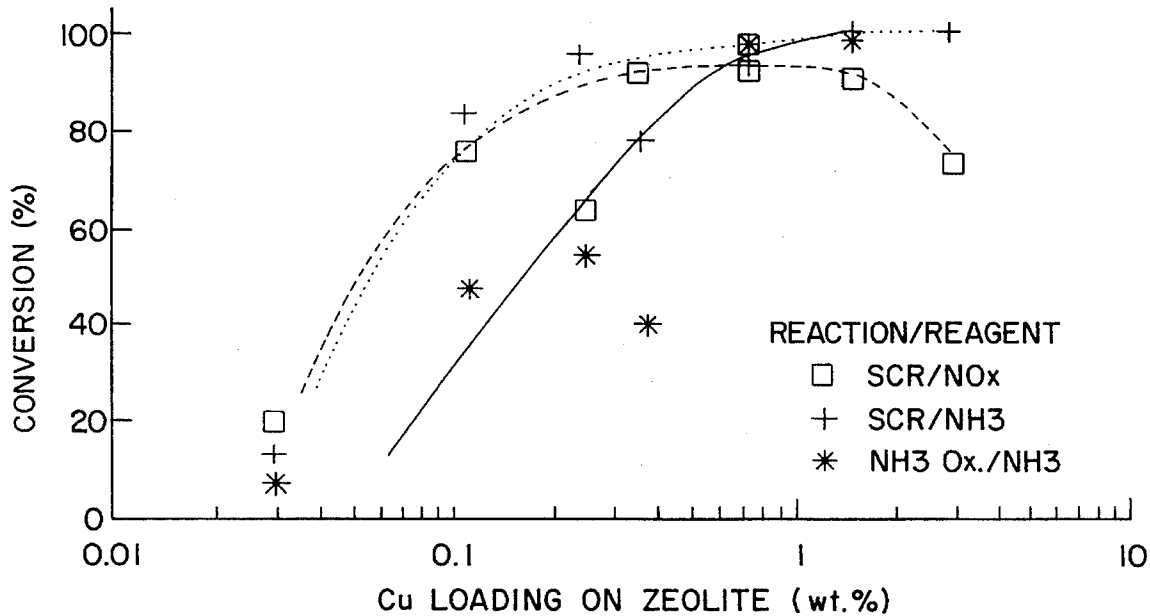
2133271	1/1973	Germany	423/213.2
2208190	8/1973	Germany	423/213.7
51-69476	6/1976	Japan .	
62-97629	5/1987	Japan	423/237
2-4453	1/1990	Japan	423/237

Primary Examiner—Gary P. Straub
Assistant Examiner—Timothy C. Vanoy

[57] **ABSTRACT**

A zeolite catalyst composition is provided in which a first or upstream zone of the catalyst has a lower metal (e.g., iron or copper) promoter loading than the metal promoter moter loading of the second or downstream zone of the catalyst. The first zone may contain from none up to about 1 percent by weight of the promoter and the second zone may contain from about 1 to 30 percent by weight promoter. The zeolite may be any suitable zeolite, especially one having a silica-to-alumina ratio of about 10 or more, and a kinetic pore size of about 7 to about 8 Angstroms with such pores being interconnected in all three crystallographic dimensions. The method of the invention provides for passing a gaseous stream containing oxygen, nitrogen oxides and ammonia sequentially through first and second catalysts as described above, the first catalyst favoring reduction of nitrogen oxides and the second catalyst favoring the oxidation or other decomposition of excess ammonia.

12 Claims, 3 Drawing Sheets



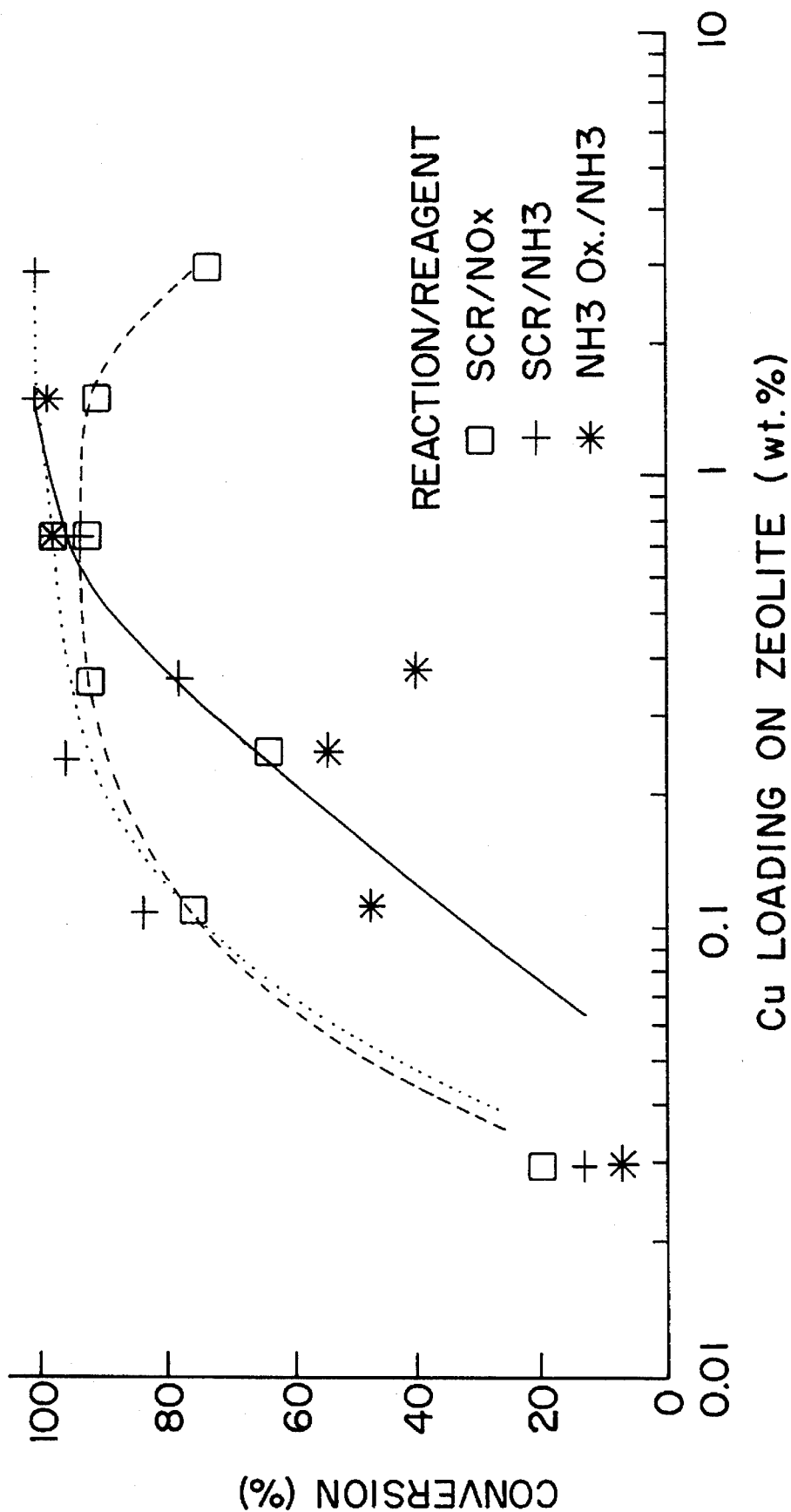


FIG. 1

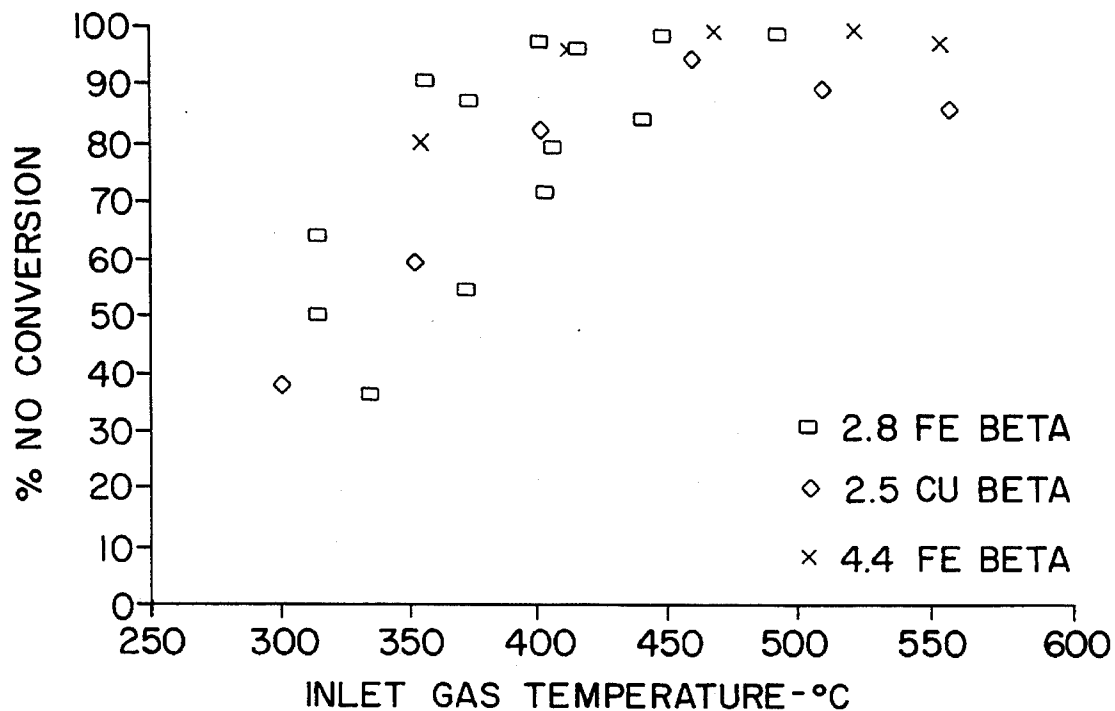


FIG. 2

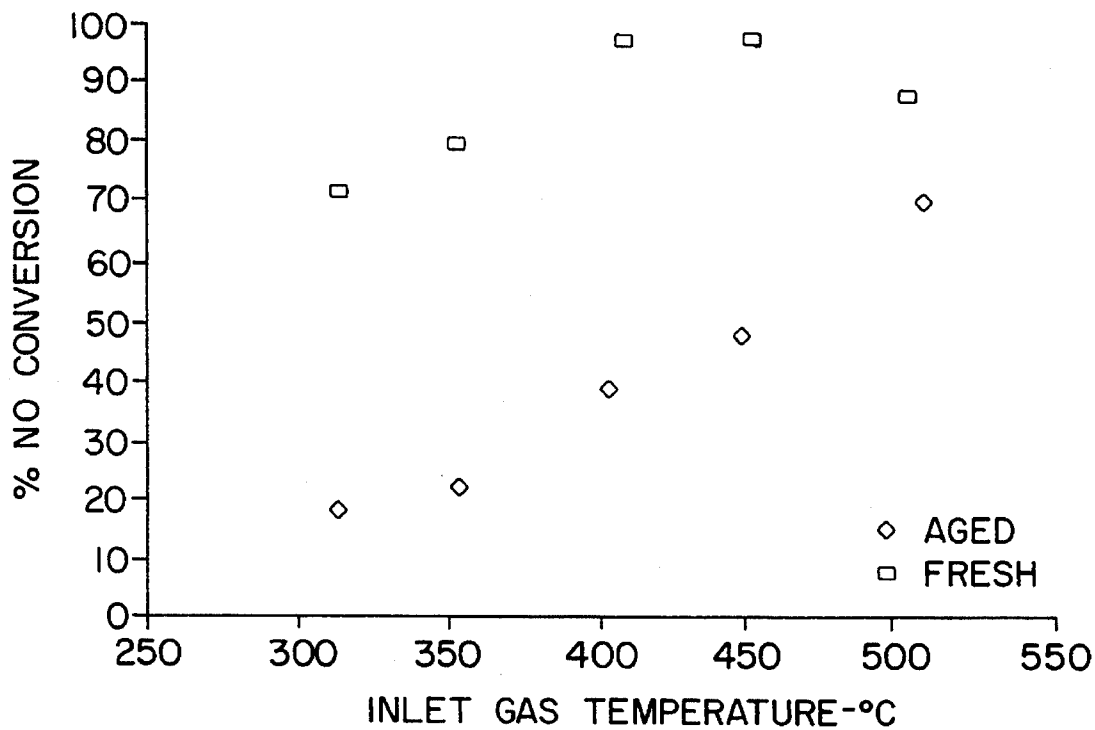


FIG. 3

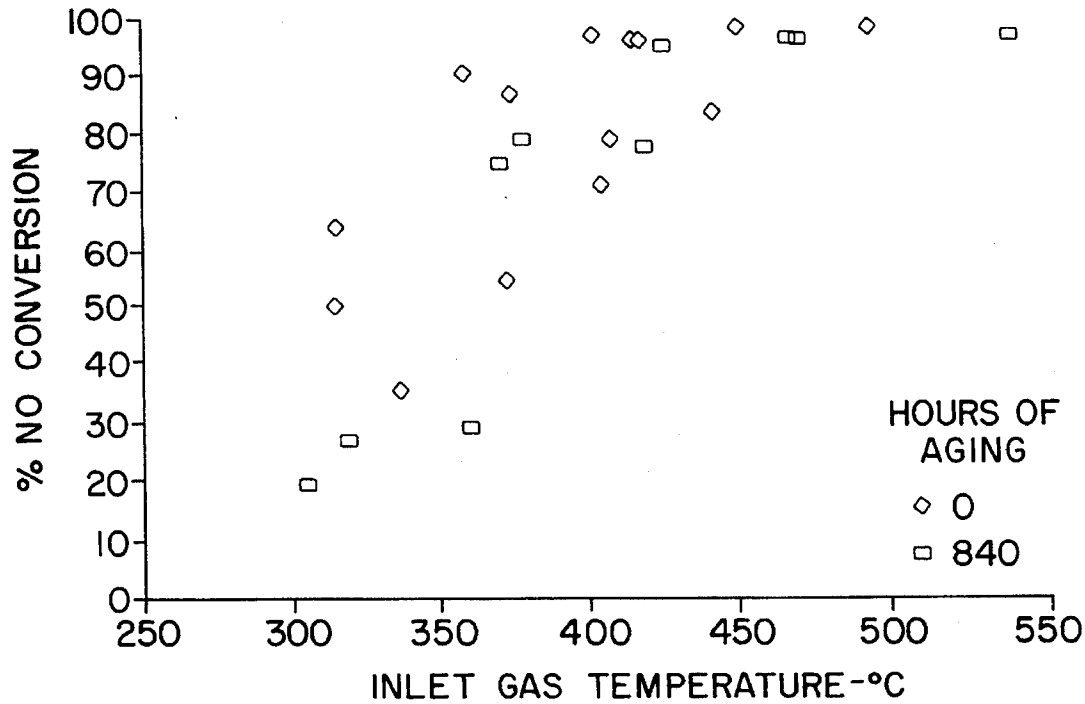


FIG. 4

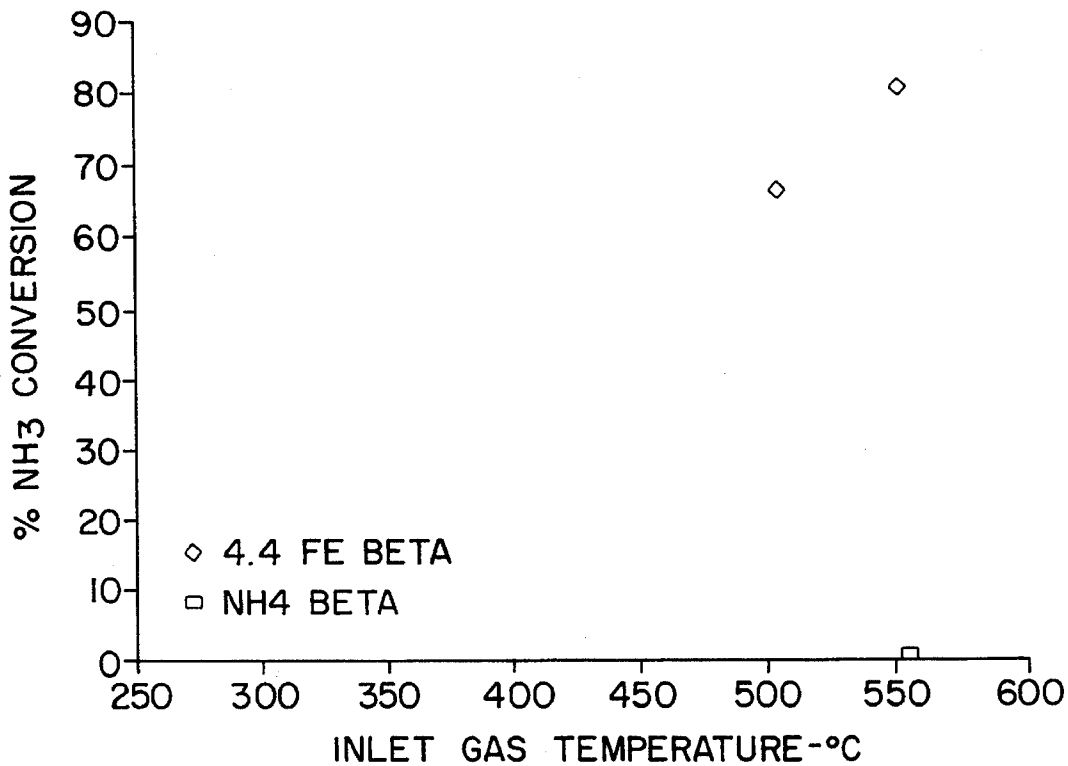


FIG. 5

**STAGED METAL-PROMOTED ZEOLITE
CATALYSTS AND METHOD FOR
CATALYTIC REDUCTION OF NITROGEN
OXIDES USING THE SAME**

This is a divisional of application Ser. No. 07/340,992 filed on Apr. 20, 1989, now U.S. Pat. No. 5,024,981.

BACKGROUND OF THE INVENTION

1. The present invention is concerned with metal-promoted zeolite catalysts and a method for the catalytic reduction of nitrogen oxides with ammonia using the catalysts, including carrying out such catalytic reduction selectively in the presence of oxygen. 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 metals including copper, vanadium, chromium, iron, cobalt or nickel, and is 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 of the Publication, it is stated that a slight decrease of the activity of a dealuminized, i.e., 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 its silica to alumina ratio.

UK Patent Application 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 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 stated to be 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.

U.S. Pat. No. 4,302,431 discloses method and apparatus for controlling the content of nitrogen oxides in gases, including a first stage of high temperature, uncatalyzed reduction of nitrogen oxides with ammonia, followed by a second, catalyzed stage in which decomposition of residual nitrogen oxides and ammonia (column 4, lines 44-49) is carried out. Example 1 discloses the use of calcium silicate plates impregnated with ferric sulfate as the catalyst, and the patentee notes (column 6, lines 36-42) that other catalysts having denitrifying capacity, such as chromium and vanadium, may also be utilized.

U.S. Pat. No. 3,970,739 discloses (column 3, lines 32-46) mixing gases obtained from an ammonia synthesis plant waste water stream with flue gases so as to provide about 0.3 to 10 moles of ammonia per mole of nitrogen oxides. The resultant gaseous mixture is contacted in a first stage with a metal catalyst to reduce nitrogen oxides and any unreacted ammonia is then decomposed in a second stage in the presence of a suitable catalyst; the process is carried out at a temperature of from 150° to 700° C. The first stage catalyst may be platinum or palladium, or oxides of copper, vanadium, molybdenum or tungsten, or a metal complex oxide such as an iron-chromium complex oxide (column 5, line 53 et seq). The second stage catalyst may be any suitable catalyst (column 7, lines 1-7) such as iron-chromium, chromium-magnesia, and chromium plus one or more of tin, antimony vanadium, cobalt phosphorus zinc, nickel, titanium, molybdenum and tungsten (column 6, line 59). Separate catalytic reactors or a single reactor containing the first and second stage catalysts in sequence, may be used.

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. The art also shows an awareness of providing a two-stage process in which, in a first stage, a thermal or catalyzed process may be used for the reduction of nitrogen oxides with ammonia and, in a second stage, residual ammonia is decomposed to nitrogen.

SUMMARY OF THE INVENTION

Generally, the present invention provides a metal-promoted zeolite catalyst and a method for using the same in the selective catalytic reduction of nitrogen oxides with ammonia, in which the promoter loading on the catalyst is staged so that the promoter loading in a first or upstream zone of the catalyst is lower than the promoter loading in a second or downstream zone of the catalyst. It has been found that by thus staging the promoter loading on a suitable zeolite

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