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(54) Title: CATALYTIC SYSTEM FOR THE REDUCTION OF NITROGEN OXIDES

(57) Abstract

A catalytic process for the treatment of exhaust containing NO_x along with other undesirable compounds is described. One embodiment of the process comprises a catalytic stage to selectively catalytically reduce NO_x over an intermediate pore size zeolite catalyst that has been treated or modified to contain iron and then has been hydrothermally treated at least one time.

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CATALYTIC SYSTEM FOR THE REDUCTION OF NITROGEN OXIDES

This invention is concerned with the abatement of nitrogen oxides and, optionally, other undesirable compounds, in industrial and engine exhaust gases. In particular, it is concerned with a catalytic method for efficiently eliminating these undesirable compounds before discharge to the atmosphere. It is more particularly concerned with the use of a specially prepared catalyst comprising an intermediate pore size zeolite that has been treated or modified to contain iron or an iron compound for the selective catalytic reduction of the NO_x present in the exhaust gas.

The present invention concerns a catalyst that is useful for treating an exhaust gas comprising NO_x and ammonia, the catalyst comprising an intermediate pore size zeolite and iron or an iron compound that has been hydrothermally treated, the hydrothermal treatment and the iron concentration being effective to produce a catalyst that is capable of converting at least 75 percent of the NO_x and ammonia present in the exhaust gas after the catalyst has been treated in 100 percent steam at a temperature of 700°C for 10 hours.

The present invention also concerns a process for treating exhaust gas comprising NO_x and ammonia comprising contacting the exhaust gas with the catalyst described above under conditions effective for the conversion of at least a portion of the NO_x and ammonia to innocuous compounds.

An embodiment of the invention is a method for treating a gas mixture comprising NO_x, ammonia, and, optionally, at least one of CO and a hydrocarbon and mixtures thereof, said method comprising directing the gas mixture along with a source of oxygen, such as air, over a catalyst under conditions effective for the selective catalytic reduction of NO_x, said catalyst comprising an

intermediate pore size zeolite which has been treated to contain iron or an iron compound, has been hydrothermally treated at least once, and optionally further comprises a binder.

As mentioned above, catalysts useful in this invention comprise intermediate pore size zeolites that have been treated or modified with iron or an iron compound. The iron may be added by ferrocene impregnation, ion-exchange under specified conditions, contacting the zeolite with a water soluble iron-containing salt or salt precursor, contacting the zeolite with another type of inorganic iron-containing compound, e.g., iron oxide, or the iron may be incorporated into the zeolite during the in-situ production of the zeolite from zeolite seeds, silica, and clay. Each of these methods will be further described below.

The term "exhaust gas" as used herein means any waste gas which is formed in an industrial process or operation and which is normally disposed of by discharge to the atmosphere, with or without additional treatment. "Exhaust gas" also includes the gas produced by internal combustion engines. The composition of such a gas varies and depends on the particular process or operation which leads to its formation.

The conversion of NO_x to N_2 is believed to proceed generally according to equations (1) and (2).

$$2\ NO_2 + 4\ NH_3 + O_2 \longrightarrow 3\ N_2 + 6\ H_2O \qquad (1)$$

$$4\ NO + 4\ NH_3 + O_2 \longrightarrow 4\ N_2 + 6\ H_2O \qquad (2)$$

This invention is effective for treating exhaust gas containing the approximate stoichiometric amount of ammonia. The ammonia may be present in the gas, may be added to the gas, or may be produced by an upstream process. As used herein, the expression "approximate stoichiometric amount of ammonia" is intended to mean 0.75 to 1.25 times the molar amount of ammonia indicated in equations (1) and (2) when excess oxygen is present.

Carbon monoxide and hydrocarbons present in the exhaust gas may be oxidized to carbon dioxide and water

over the catalyst. Additionally, hydrocarbons may be selectively absorbed/adsorbed on the catalyst.

Feeds

This invention is effective to treat industrial and engine exhaust gases to remove NO_x, and optionally other undesirable compounds, such as CO and hydrocarbons, if present. These exhaust gases are typically produced in internal combustion engines, and coal or gas-fired or oil-fired furnaces, boilers and incinerators, and by the manufacture of nitric acid, by the nitration of organic chemicals, and by other chemical operations such as the reprocessing of spent nuclear fuel rods by dissolution in nitric acid to recover uranyl nitrate followed by calcination to convert the nitrate to uranium oxide.

Process Conditions

The exhaust gas may be treated in the catalytic system of this invention at a temperature of 200°C to 1,000°C or more, e.g., within the range of 225°C to 900°C, e.g., of 225°C to 750°C, e.g., of 250°C to 600°C and at a gas hourly space velocity, GHSV, (vols. of gas at STP per volume of catalyst per hour) adjusted to provide the desired conversion. The GHSV can be from 1,000 to 500,000 hr^{-1}, e.g., within the range of 2,500 to 250,000 hr^{-1}, e.g., from 5,000 to 150,000 hr^{-1}, e.g., from 10,000 to 100,000 hr^{-1}. The process of this invention may be operated at subatmospheric to superatmospheric pressure, e.g. at 34.5 to 3,450 kPaa (5 to 500 psia), e.g., at 68.9 to 345 kPaa (10 to 50 psia), i.e. near or slightly above atmospheric pressure.

The gas mixture directed over the catalyst may contain at least a stoichiometric amount of oxygen as indicated by equations (1) and (2) above. Excess levels of oxygen above the stoichiometric amount may be desirable. In the method of this invention, a source of oxygen, such as air, is co-fed over the catalyst along with the exhaust gas. If

sufficient oxygen is not present in the exhaust gas, a source of oxygen, e.g. air, may be added to the exhaust gas, and if sufficient oxygen is present in the exhaust gas, no air need be added to the exhaust gas.

Adequate conversion may be readily achieved with a simple stationary fixed-bed of catalyst. However, other contacting means are also contemplated, such as contacting with a fluid bed, a transport bed, and a monolithic catalyst structure such as a honeycomb. Suitable mixing may be used in the exhaust gas before the treatment according to the present invention to produce a homogeneous gas mixture for treatment.

Catalyst Composition

Catalysts useful in this invention may comprise an active material and a support or binder. The support for the catalysts of this invention may be the same as the active material and further can be a synthetic or naturally occurring substance as well as an inorganic material such as clay, silica, zirconia, titania and/or one or more other metal oxides. One binder that is suitable is a low acidity titania prepared from a mixture comprising a low acidity titanium oxide binder material and an aqueous slurry of titanium oxide hydrate. The preferred support is one that is a high surface area material that also possesses a high temperature stability and further possesses a high oxidation stability.

The binder may be prepared according to methods disclosed in U.S. Patent Nos. 5,430,000; 4,631,267; 4,631,268; 4,637,995; and 4,657,880. Also, the catalysts described herein may be combined with any of the binder precursors described in the above application and patents, and then may be formed, such as by extrusion, into the shape desired, and then hydrothermally treated and/or calcined as hereinafter described. The preferred binder may include less than 50 weight percent alumina, e.g., less than 2 weight percent alumina, e.g., is substantially free

of alumina. By the term "substantially free of alumina" is meant that no alumina is intentionally added to the binder, however, it is recognized that trace amounts of alumina may be present.

When low acidity titania is used as a binder, it may be desirable that the formable, e.g., extrudable, mass prepared by combining the zeolite, the iron salt, and the titania binder precursors contain at least 0.5 wt.%, e.g., 1 wt.% to 20 wt.%, e.g., 2 to 8 wt.% of the aqueous slurry of titanium oxide hydrate.

The low acidity titania may be added in dry particulate form, e.g., titanium oxide hydrate, so as to control the moisture content of the binder/dispersant mixture at a level to promote satisfactory forming, e.g., extrusion.

The catalysts may also contain stabilizers such as alkaline earth oxides, phosphates and combinations thereof.

Catalysts useful in invention are frequently used with a substrate. A material can be both substrate and part of the catalyst. The catalyst may be combined with the substrate in any method that ensures that the catalyst will remain intact during the catalytic reaction, e,g., the catalyst may be present as a coating on the substrate, or it can be present as an integral part of the substrate.

The catalyst useful in this invention will now be described in detail. It comprises an intermediate pore size zeolite (e.g., less than 7 Angstroms pore size, such as from 5 to less than 7 Angstroms) having a silica to alumina molar ratio of at least 5, e.g., at least 20, e.g., between 40 and 1000, e.g., 50 to 500, a Constraint Index of 1 to 12, said zeolite having been treated or modified to contain iron or a iron compound. The Constraint Index qualifies it as having an intermediate pore size. The method by which Constraint Index is determined is described fully in U.S. Pat. No. 4,016,218.

Examples of such zeolites include ZSM-5 (U.S. Patent No. 3,702,886 and Re. 29,948); ZSM-11 (U.S. Patent No.

3,709,979); ZSM-12 (U.S. Patent No. 3,832,449); ZSM-21 (U.S. Patent No. 4,046,859); ZSM-22 (U.S. Patent No. 4,556,477); ZSM-23 (U.S. Patent No. 4,076,842); ZSM-35 (U.S. Patent No. 4,016,245); ZSM-38 (U.S. Patent No. 4,406,859); ZSM-48 (U.S. Patent No. 4,397,827); ZSM-57 (U.S. Patent No. 4,046,685); and ZSM-58 (U.S. Patent No. 4,417,780).

A catalyst useful in the method of this invention may be prepared by combining a zeolite, such as HZSM-5, an iron salt or other iron containing compound, a high molecular weight, hydroxy functional silicone, such as Dow Corning Q6-2230 silicone resin, a suitable extrusion aid, such as methyl cellulose, and a suitable polar, water soluble carrier, such as methanol, ethanol, isopropyl alcohol, N-methyl pyrrolidone or a dibasic ester along with water as needed, then forming the mixture into the desired shape, such as by extrusion, then simultaneously calcining and hydrothermally treating the formed material. One particular methyl cellulose that is effective as an extrusion aid in the method of this invention is a hydroxypropyl methyl cellulose, such as K75M Methocel™, available from Dow Chemical Co. Dibasic esters that are useful in this invention include dimethyl glutarate, dimethyl succinate, dimethyl adipate, and mixtures thereof, one example of which is DuPont Chemical Co. DBE, which typically comprises 50 to 75 percent dimethyl glutarate, 10 to 25 percent dimethyl adipate, 19 to 26 percent dimethyl succinate and less than 0.2 wt.% methanol. Other silicone resins that may be used in the method of this invention include those described in U.S. Patent No. 3,090,691.

The relative proportions of zeolite component and the support material on an anhydrous basis may vary widely with the zeolite content ranging from between 5 to 99 percent by weight and more usually in the range of 10 to 95 percent by weight, specifically from 20 to 90 percent by weight of the dry composite.

Original ions, e.g., alkali or alkaline earth metal, of the as-synthesized intermediate pore size material and any found in the zeolite/support material can be replaced in accordance with techniques well known in the art, at least in part, by ion-exchange with other ions. For the present catalyst composition, preferred replacing ions include hydrogen ions and hydrogen precursor, e.g., ammonium ions. ZSM-5 in the hydrogen exchanged form is referred to herein as HZSM-5. Representative ion-exchange techniques are disclosed in a wide variety of patents including U.S. Patents 3,140,249; 3,140,251; and 3,140,253.

The desired iron loading on the zeolite component of the catalyst is 0.01 to 5 wt.%, e.g., at least 0.4 wt.%, e.g., at least 0.6 wt.%, e.g., at least 1 wt.%, e.g., at least 1.5 wt.%, preferably 2 wt.%, iron into the zeolite. The catalyst may also optionally include another metal, such as a transition metal, preferably a noble metal, the combination of the metals being able to oxidize other undesirable compounds present in the exhaust gas along with allowing the SCR of NO_x. The metal may be at least one of copper, zinc, vanadium, chromium, manganese, cobalt, nickel, palladium, platinum, molybdenum, tungsten, sodium, potassium, magnesium, calcium, barium, cerium and mixtures thereof, with the noble metals, platinum, palladium and combinations of these, along with cerium, particularly preferred. The terms "metal" and "iron" as used herein are intended to include the elemental metal as well as metal oxides, metal sulfides, and other metal containing compounds.

After the intermediate pore size zeolites have been treated or modified to contain iron or an iron compound, they may be washed with water and dried at a temperature ranging from 65°C to 315°C. They may also be calcined or thermally treated in air, or in an inert gas, at temperatures ranging from 260°C to 925°C for periods of time ranging from 1 to 48 hours or more, typically at 538°C

for 4 to 6 hours. While subatmospheric or superatmospheric pressure can be employed for the thermal treatment, atmospheric pressure is preferred simply for reasons of convenience.

Catalysts of improved selectivity and other beneficial properties, such as improved resistance to ageing in an atmosphere containing steam, can be obtained by subjecting the iron containing zeolite to at least one treatment with streams containing steam (hydrothermally treating the catalysts) at elevated temperatures ranging from 260°C to 900°C, e.g., 400°C to 850°C, e.g., 500°C to 750°C. The hydrothermal treatment may be accomplished in an atmosphere containing at least 20 ppm, 0.5%, 5, 10%, 20%, even up to 99% steam in air or some other suitable gas stream or in an atmosphere consisting of steam or nitrogen and some other gas which is essentially inert to the zeolite. Optionally, more than one hydrothermal treatment may be used, specifically two, three, or more hydrothermal treatments at different temperatures, e.g., increasing temperatures, may be used. Examples of steaming conditions include 600°C with 10 percent steam in air for 10 hours, 700 to 750°C with 5 to 10 percent steam in air for 6 to 10 hours, and 850°C with 20 percent steam in air for 6 hours. Typical steaming conditions are described in U.S. Patent Nos. 4,429,176; 4,522,929; 4,594,146; and 4,663,492. The calcination and hydrothermal treatments of the catalysts are preferably combined into one treatment step and conducted simultaneously.

As mentioned above, the iron may be added to the catalyst by ferrocene impregnation, ion-exchange under specified conditions, contacting the zeolite with an inorganic iron-containing salt or salt precursor, contacting the zeolite with another type of inorganic iron-containing compound, e.g., iron powder or iron oxide, or the iron may be incorporated into the zeolite during the in-situ production of the zeolite from zeolite seeds, silica, and clay.

Ferrocene impregnated catalysts may be prepared by contacting the zeolite with ferrocene which has been dissolved in a suitable solvent. Suitable solvents are those which dissolve the ferrocene and may then be removed from the impregnated zeolite under conditions sufficiently mild as to avoid causing the ferrocene to sublimate off the zeolite. Examples of suitable organic solvents include benzene, toluene, xylenes, and hexane among others. The impregnation is typically conducted for more than 4 hours, specifically from 4 hours to several days, more specifically from 6 hours to 100 hours. The impregnation is generally conducted at conditions effective to achieve the desired iron loading or iron concentration on the zeolite.

The impregnation may occur either before or after the zeolite is combined with the support. For example, if the zeolite is first combined with the support and then impregnated, ferrocene that is deposited on the surface of the zeolite and on the support may be washed off using a solvent having an effective atomic diameter that is larger than the zeolite pore size, e.g., an organic solvent such as Tetralin®.

The impregnation may be conducted after first drying or dehydrating the zeolite. Also, the ferrocene solution may be prepared using a water-free or dry solvent.

The impregnated zeolite is recovered by removing the solvent from the zeolite. It is desired to remove the solvent without causing the ferrocene to sublimate off the zeolite. One possible way is to evaporate the solvent at a temperature less than the ferrocene sublimation temperature, 100°C. This solvent removal may be done at superatmospheric pressure, if desired, or pressures ranging from subatmospheric to atmospheric. The recovered ferrocene impregnated zeolite then may be calcined at 450°C to 550°C to oxidize the ferrocene and to convert the iron to its oxide.

Another catalyst comprises an intermediate pore size zeolite which has been exposed to at least one ion-exchange sequence under specific conditions, wherein the ion-exchange sequence comprises the steps of contacting the intermediate pore size zeolite with an aqueous solution of a ferrous, Fe(II), salt under suitable conditions, recovering the zeolite, and calcining the zeolite. The conditions include those effective to substantially prevent oxidation of the ferrous ion to the ferric form, such as using nitrogen, argon and the like inert gases to blanket the solution. The conditions also include stirring or mixing at a temperature of above 55°C, specifically above 65°C, or those temperatures effective to reduce the hydration sphere of the ferrous cation to a size small enough to enter the pores of the zeolite. The ferrous cation is reported to have an ionic radius in an aqueous solution of about 0.0000000006 meters (6 Å) at 25°C, which is too large to enter ZSM-5 pores, which are slightly smaller than this. Increasing temperature is believed to reduce the size of the hydration sphere associated with the ferrous cation. For example, with increasing temperature, a ferrous compound, ferrous sulfate, changes from the heptahydrate form to the tetrahydrate form (at 56.6°C) and then to the monohydrate form (at 65°C).

The ion-exchange may be conducted for more than 4 hours, e.g., from 4 hours to several days, e.g., from 6 hours to 100 hours. During the ion-exchange, the pH of the aqueous solution may be maintained between 1 and 4.5 or at a pH level effective to prevent precipitation of the ferrous salt.

It has been found that ferrous, Fe(II), ions are more readily exchanged into the zeolite than ferric, Fe(III), ions.

Ferrous, Fe(II), salts useful in this invention include the water soluble salts, such as, ferrous ammonium sulfate, ferrous chloride, ferrous fluosilicate, ferrous hyposulfite, ferrous iodide, ferrous lactate, ferrous

nitrate, ferrous perchlorate, ferrous sulfate, and ferrous thiocyanate.

After the iron has been ion-exchanged into the zeolite, the zeolite may be recovered by cooling the aqueous solution below 55°C to 65°C, filtering the zeolite from the aqueous solution and washing the filtered zeolite with a neutral or slightly basic solvent, for example, an aqueous solvent with a pH of from 6 to 9, such as distilled or deionized water. The solvent washing may be conducted at conditions effective to avoid leaching the iron from the zeolite. The aqueous solution and the ion-exchanged zeolite need not be maintained under inert conditions after the solution has been cooled. The recovered zeolite may be dried, calcined and hydrothermally treated as more fully described herein.

The ion-exchange sequence described above may be conducted at least once, e.g., at least twice, e.g., at least three times, e.g., four or more times.

Another method to incorporate iron onto the zeolite is to contact an intermediate pore size zeolite with an iron salt or salt precursor. In this method, the iron salt may first be dissolved in water or another suitable solvent and then the zeolite may be contacted with the solution. Alternatively, the iron salt and the zeolite, and any binder material desired, may be physically combined and then water or another suitable solvent added and the mixture recovered and formed, as desired. The formed material may be dried, calcined, or hydrothermally treated as is more fully described herein. As will be apparent to one skilled in the art, any method that is effective to contact the zeolite with the iron salt and to achieve a high degree of iron distribution on and inside the zeolite may be used, including, but not limited to an incipient wetness technique.

Suitable iron salts include all of the ferrous salts mentioned above, as well as ferric acetate, iron(III) benzoate, iron(III) cacodylate, iron(III) dichromate,

iron(III) citrate, iron(III) fluoride, iron(III) fluosilicate, iron(III) formate, iron(III) glycerophosphate, iron(III) hydrogen cyanide, iron(III) hydrosulfate, iron(III) lactate, iron(III) malate, iron(III) oxalate, iron(III) orthosphosphate, iron(III) hypophosphite, iron(III) sulfide, iron(III) thiocyanate, ferric acetylacetonate, ferric ammoniumchloride, ferric chloride, iron(III) nitrate nanohydrate, iron(III) sulfate pentahydrate, ammonium ferric sulfate, ferric bromide, ferric iodide, and any other ferrous, ferric, or other iron salts that are water soluble. Also included are precursors of all of the salts mentioned above.

The incorporation of iron onto the zeolite may be accomplished by contacting an intermediate pore size zeolite with an iron salt or salt precursor, such as those mentioned above. In this method, the iron salt may first be dissolved in water or another suitable carrier or solvent and then the zeolite may be contacted with the solution, recovered from the solution, dried and then bound if desired. Alternatively, the iron salt and the zeolite, and any binder material desired, may be physically combined with water or another suitable carrier or solvent to produce a mixture and the mixture recovered and formed, such as by extrusion. The formed material may be dried, calcined, or hydrothermally treated as is more fully described herein. As will be apparent to one skilled in the art, any method that is effective to contact the zeolite with the iron salt may be used, including, but not limited to mulling or an incipient wetness technique.

Yet another method that is suitable to add iron to the zeolite is to physically contact an intermediate pore size zeolite with an inorganic iron-containing compound, e.g., iron oxide. In this method, it is preferred to use a finely divided iron-containing compound, such as a fine pigment grade red iron oxide. It is also preferred to add a binder precursor to the physical mixture of the iron-containing compound and the zeolite and to form the

physical mixture. After the desired shape has been formed, the iron-contacted zeolite may be calcined and hydrothermally treated as is more fully described herein.

Another catalyst may be prepared by in-situ crystallization of an aggregate, e.g., a preformed clay aggregate. The aggregate comprises four components: seeds of an intermediate pore size zeolite, e.g., ZSM-5 seeds, silica, e.g., a colloidal silica such as Ludox™ available from E. I. DuPont de Nemours & Co., clay, and iron oxide. Optionally, the aggregate can also include alumina. Various techniques for preparing an in-situ crystallized zeolite are described in U.S. Patent Nos. 4,522,705; 4,091,007; and 4,800,187.

The zeolite may be prepared from a clay aggregate which comprises a non-clay added source of silica. The sources of silica in the reaction mixture may include both a clay and a non-clay source of silica, or a clay alone. Non-clay sources of silica that can be employed in the synthesis are Ludox™, an aqueous dispersion of colloidal silica, water glass, sand, silica gel, fused silica, and finely-divided precipitated silicas, such as Hi-Sil, Quso, and Zeosil 100.

The clay component which is treated to form the zeolite-containing catalyst can be selected from the group consisting of kaolin, halloysite, montmorillonite, illite, and dickite, with kaolin preferred.

The preformed aggregate may be treated for one or more hours at a temperature sufficient to convert the clay into the metakaolin phase, e.g., greater than 927°C to 1000°C. After the thermal treatment of the aggregate, the zeolite may be crystallized by treatment at a temperature of greater than 135°C, e.g., 149°C, in the presence of water, alkali metal cations, and optionally, a directing agent such as tetraalkylammonium ions, e.g., a tetraalkylammonium halide, such as tetrapropylammonium bromide, or a n-alkylamine, such as n-propylamine, with no additional nutrients for zeolite formation.

The in-situ formed zeolite may be prepared from a aggregate comprising about 3-5% zeolite seeds, e.g., ZSM-5 seeds; 23-25% silica, e.g. colloidal silica; 68-70% clay, e.g., kaolin clay; and 0.01-5% metal oxide, e.g., iron oxide.

As noted above, the catalytic reduction of nitrogen oxides is substantially effected by the use of the present process. By substantially effected is meant a conversion of greater than 40, 75, 80, 85, 90, 95, or even 99% or more of the nitrogen oxides and the ammonia in the exhaust gas to innocuous compounds, such as nitrogen, through the use of this process. This is also referred to herein as conversion of a substantial portion of the NO_x and ammonia in the exhaust gas to innocuous compounds.

Example 1

Base ZSM-5

A HZSM-5 sample, prepared according to U.S. Patent No. 3,702,886, was used as the reference sample and was used as the basis for all of the other examples.

Example 2

Preparation of an iron containing ZSM-5

An iron containing ZSM-5 sample was prepared by the following method: 100 g of distilled water was heated to about 85°C with constant stirring under a blanket of dry nitrogen. Approximately 0.11 g of ferrous sulfate and 5.1 g of the same HZSM-5 as Example 1 were added to the heated water. A solution pH of about 2 was maintained by dropwise addition of nitric acid or ammonium hydroxide, as needed. The exchange solution was maintained at about 85°C under a nitrogen blanket with continued stirring for approximately 17 hours. The solution was subsequently cooled to room temperature, filtered and washed with distilled water. The filtered solid was calcined in air for 8 hours at 538°C to produce the iron containing catalyst, Catalyst A. The iron loading of this catalyst as prepared is about 0.5 wt.%.

Example 3

Comparative testing against the base ZSM-5

In this example, the SCR activity of Catalyst A is compared with the base HZSM-5 catalyst from Example 1. The catalyst samples were evaluated using a fixed bed quartz reactor operating between 250-550°C. The reactor inlet contained 500 ppm NO, 500 ppm NH_3, and 5 vol.% O_2 in a He carrier flowing at a constant gas hourly space velocity (GHSV) of 12,000 hr^{-1}. The effluent from the reactor was continuously monitored by non-dispersive infrared spectroscopy (NDIR) detectors. Catalyst activity results are reported below in Table 1.

Table 1

Percent N in Feed Converted to N_2

Temperature, °C	Base ZSM-5 Catalyst	Catalyst A
550	89%	93%
455	100%	98%
400	100%	98%
345	71%	97%
250	26%	92%

Example 4

Preparation of an Iron Containing ZSM-5

An iron containing ZSM-5 sample was prepared by the following method: a solution containing 25 g of the same HZSM-5 as Example 1 and 500 g of distilled water was heated to about 77°C with constant stirring under a blanket of dry argon. Approximately 0.3 g of ammonium ferrous sulfate was added to the heated solution. A solution pH of 3 was maintained by dropwise addition of nitric acid or ammonium hydroxide, as needed. The exchange solution was maintained at about 77°C under an argon blanket with continuous stirring for approximately 9 hours. The solution was subsequently cooled to room temperature, filtered and

washed with distilled water. The filtered solid was calcined in air for 8 hours at 538°C to produce the iron containing catalyst, Catalyst B. The iron loading of this catalyst as prepared is about 0.5 wt.%.

Example 5

Comparative testing against a base ZSM-5

In this example, the SCR activity of Catalyst B is compared with the base HZSM-5 catalyst from Example 1. The catalyst samples were evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 2.

Table 2

Percent N in Feed Converted to N_2

Temperature, °C	Base ZSM-5 Catalyst	Catalyst B
550	89%	100%
455	100%	100%
400	100%	100%
345	71%	100%
250	26%	90%

Example 6

Preparation of an Iron Containing ZSM-5

An iron containing ZSM-5 sample was prepared by the following method: a solution containing 0.2354 g of ferrous acetate in 30 g distilled water was added to a flask containing 15 g of the same HZSM-5 as Example 1 at room temperature. The catalyst slurry was mixed for approximately 2 hours and was air dried at room temperature for about 16 hours. The dried catalyst was calcined in air for 8 hours at 538°C to produce the iron containing catalyst, Catalyst C. The iron loading of this catalyst as prepared is about 0.5 wt.%.

Example 7

Comparative testing against a base ZSM-5 and Catalyst A

In this example, the SCR activity of Catalyst C is compared with the base HZSM-5 catalyst from Example 1 and Catalyst A as prepared in Example 2. The catalyst samples were evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 3.

Table 3

Percent N in Feed Converted to N_2

Temperature, °C	Base Catalyst	Catalyst A	Catalyst C
550	89%	93%	89%
455	100%	98%	91%
400	100%	98%	91%
345	71%	97%	90%
250	26%	92%	85%

Example 8

Preparation of an iron containing HZSM-5

An iron containing ZSM-5 catalyst was prepared by the following method: 7.6 g of the same HZSM-5 as that of Example 1 was heated in a stream of dry nitrogen to 375°C. After this temperature was maintained for 4 hours, the catalyst was cooled, in a stream of dry nitrogen, to room temperature. A solution of 0.5 g of ferrocene (dicyclopentadienyliron) in 30 g dry benzene was then added to the calcined zeolite and the slurry allowed to mix on a roller for about 16 hours. The benzene was allowed to evaporate at room temperature to give a benzene/ferrocene wetted zeolite. This wet solid was then heated to a temperature that did not exceed 100°C in a vacuum oven so as to remove the residual benzene. This dry catalyst was then calcined in a stream of air at about 450°C for about 6

hours to produce the desired iron containing catalyst, Catalyst D. The iron loading of this catalyst is about 1.8 wt.%.

Example 9

Catalytic evaluation of Catalyst D

In this example, the SCR activity of Catalyst D from Example 8 was evaluated. The catalyst sample was evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 4.

Table 4

Percent N in Feed Converted to N_2

Temperature, °C	Catalyst D
550	90%
455	97%
400	98%
345	98%
250	95%

Example 10

Preparation of an iron containing HZSM-5

An iron containing ZSM-5 catalyst was prepared by the following method: about 10 g of the same HZSM-5 as that of Example 1 was heated in a stream of dry air to 375°C for 4 hours and then was cooled to room temperature. A solution of 0.1667 g of ferrocene (dicyclopentadienyliron) in 30 g dry toluene was then added to the dried zeolite and the slurry was mixed at room temperature overnight. Excess toluene was allowed to evaporate at room temperature to give a toluene/ferrocene wetted zeolite. The recovered solid was then calcined in a stream of dry air at about 538°C for about 6 hours to produce the desired iron containing catalyst, Catalyst E. The iron loading of this catalyst is about 0.45 wt.%.

Example 11

Catalytic evaluation of Catalyst E

In this example, the SCR activity of Catalyst E from Example 10 was evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 5.

Table 5

Percent N in Feed Converted to N_2

Temperature, °C	Catalyst E
550	98%
455	99%
400	99%
345	98%
250	81%

Example 12

Preparation of an iron containing HZSM-5

An iron containing ZSM-5 catalyst was prepared by the following method: about 10 g of the same HZSM-5 as that of Example 1 was heated in a stream of dry air to 375°C for 4 hours and then was cooled to room temperature. A solution of 0.3331 g of ferrocene (dicyclopentadienyliron) in 30 g dry toluene was then added to the dried zeolite and the slurry was mixed at room temperature overnight. The slurry was filtered and washed once with 100 ml of Tetralin® to remove excess ferrocene from the external surface of the zeolite. Excess Tetralin® was allowed to evaporate at room temperature to give a Tetralin®/ferrocene wetted zeolite. The recovered solid was then calcined in a stream of dry air at about 538°C for about 6 hours to produce the desired iron containing catalyst, Catalyst F. The iron loading of this catalyst is about 0.66 wt.%.

Example 13

Catalytic evaluation of Catalyst F

In this example, the SCR activity of Catalyst F from Example 12 was evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 6.

Table 6

Percent N in Feed Converted to N_2

Temperature, °C	Catalyst F
550	96%
455	98%
400	98%
345	96%
250	88%

Example 14

Preparation of an iron containing HZSM-5

An iron containing ZSM-5 catalyst was prepared by the following method: about 10 g of the same HZSM-5 as that of Example 1 was heated in a stream of dry air to 375°C for 4 hours and then was cooled to room temperature. A solution of 0.3331 g of ferrocene (dicyclopentadienyliron) in 30 g dry toluene was then added to the dried zeolite and the slurry was mixed at room temperature overnight. Excess toluene was allowed to evaporate at room temperature to give a toluene/ferrocene wetted zeolite. The recovered solid was then calcined in a stream of dry air at about 538°C for about 6 hours to produce the desired iron containing catalyst, Catalyst G. The iron loading of this catalyst is about 1.05 wt.%.

Example 15

Catalytic evaluation of Catalyst G

In this example, the SCR activity of Catalyst G from Example 14 was evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 7.

Table 7

Percent N in Feed Converted to N_2

Temperature, °C	Catalyst G
550	95%
455	98%
400	98%
345	97%
250	91%

Example 16

Aging of the HZSM-5 catalysts

The base HZSM-5 of Example 1 and Catalysts D through G as prepared above in Examples 8, 10, 12, and 14 were hydrothermally aged. Approximately 5 g of each catalyst was placed in individual identical crucibles and put in a controlled atmosphere furnace. The furnace was continuously purged with air containing 20 wt.% water vapor. The samples were treated in this moist atmosphere at 850°C for 6 hours. The treated samples will be referred to as aged base HZSM-5, and aged Catalysts D through G.

Example 17

Catalytic evaluation of aged base HZSM-5

In this example, the SCR activity of the aged base HZSM-5 from Example 16 was evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 8.

Table 8

Percent N in Feed Converted to N_2

Temperature, °C	Aged base HZSM-5
550	82%
455	56%
400	36%
345	20%
250	9%

Example 18

Catalytic evaluation of aged Catalyst D

In this example, the SCR activity of the aged Catalyst D from Example 16 was evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 9.

Table 9

Percent N in Feed Converted to N_2

Temperature, °C	Aged Catalyst D
550	98%
455	100%
400	100%
345	98%
250	96%

Example 19

Catalytic evaluation of aged Catalyst E

In this example, the SCR activity of the aged Catalyst E from Example 16 was evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 10.

Table 10

Percent N in Feed Converted to N_2

Temperature, °C	Aged Catalyst E
550	98%
455	100%
400	99%
345	88%
250	37%

Example 20

Catalytic evaluation of aged Catalyst F

In this example, the SCR activity of the aged Catalyst F from Example 16 was evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 11.

Table 11

Percent N in Feed Converted to N_2

Temperature, °C	Aged Catalyst F
550	98%
455	99%
400	92%
345	57%
250	27%

Example 21

Catalytic evaluation of aged Catalyst G

In this example, the SCR activity of the aged Catalyst G from Example 16 was evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 12.

Table 12

Percent N in Feed Converted to N_2

Temperature, °C	Aged Catalyst G
550	97%
455	100%
400	99%
345	90%
250	33%

Example 22

Preparation of an iron containing ZSM-5

An iron containing ZSM-5 catalyst was prepared by the following method: about 20 g of ammonium iron(III) sulfate was dissolved in 74 g distilled water. This solution was added to about 120 g of the base HZSM-5 and the slurry was mixed at about room temperature and was then dried at about 100°C overnight. Approximately 10 g of the dried, impregnated solid was then calcined in air at about 600°C with about 10% steam for about 10 hours to produce the desired iron containing catalyst, Catalyst H. The iron loading of this catalyst is about 2 wt.%.

Example 23

Catalytic evaluation of Catalyst H

In this example, the SCR activity of Catalyst H from Example 22 was evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 13.

Table 13

Percent N in Feed Converted to N_2

Temperature, °C	Catalyst H
550	76%
455	95%
400	99%
345	98%
250	90%

Example 24

Preparation of an iron containing ZSM-5

An iron containing ZSM-5 catalyst was prepared by the following method: about 1.5 g of iron(III) nitrate was dissolved in 6.5 g distilled water. This solution was added to about 10 g of the base HZSM-5 and the slurry was mixed at about room temperature and was then dried at about 100°C overnight. The dried, impregnated solid was then calcined in air at about 600°C with about 10% steam for about 10 hours to produce the desired iron containing catalyst, Catalyst I. The iron loading of this catalyst is about 2 wt.%.

Example 25

Catalytic evaluation of Catalyst I

In this example, the SCR activity of Catalyst I from Example 24 was evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 14.

Table 14

Percent N in Feed Converted to N_2

Temperature, °C	Catalyst I
550	86%
455	97%
400	99%
345	99%
250	92%

Example 26

Preparation of a silica bound-iron containing ZSM-5

A silica bound iron containing ZSM-5 catalyst was prepared by the following method: about 100 g of the dried, iron impregnated HZSM-5 catalyst prepared in Example 22 was dry blended with about 22 g of Dow Corning silicone resin (Q6-2230) and about 6.8 g of K75M Methocel™ (available from Dow Chemical Co.). Approximately 89 ml of a 1:1 by volume mixture of water:isopropyl alcohol was then added to the dry blended powder. The slurry was mulled for a minimum of 5 minutes until the mixture reached the proper consistency for extrusion. The mixture was then extruded into 1/16 inch diameter cylindrical strands in a screw extruder and was allowed to dry. Approximately 10 g of the dried extrudate was calcined in air at 600°C with 10% steam for 10 hours to produce the desired iron containing catalyst, Catalyst J. The iron loading of this catalyst is about 2 wt.%.

Example 27

Catalytic evaluation of Catalyst J

In this example, the SCR activity of Catalyst J from Example 26 was evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 15.

Table 15

Percent N in Feed Converted to N_2

Temperature, °C	Catalyst J
550	74%
455	97%
400	100%
345	99%
250	88%

Example 28

Comparative testing after steaming

In this example, the SCR activity of the base HZSM-5, and Catalysts H, I, and J are compared after each of the catalyst were treated with 100% steam at 700°C for 7 hours. The catalyst samples were evaluated using similar equipment and the same procedure as Example 3. Catalyst activity results are reported below in Table 16.

Table 16

Percent N in Feed Converted to N_2

	Steamed Catalysts			
Temp., °C	Base Catalyst	Catalyst H	Catalyst I	Catalyst J
550	56%	92%	98%	92%
455	46%	100%	98%	100%
400	36%	100%	97%	100%
345	20%	100%	99%	100%
250	6%	96%	77%	95%

Example 29

An iron containing ZSM-5 catalyst was prepared by the following method: Approximately 1.5g of iron (III) nitrate was dissolved in 6.5g distilled water. This solution was

added to about 10g of the base HZSM-5 and the resulting slurry was mixed and dried at room temperature overnight. The dried inpregnated solid was then calcined in air at 600°C with 10% steam for 10 hours to produce the desired catalyst, Catalyst K. The nominal iron loading of this sample is about 2 wt%.

Example 30

In this example, the SCR activity of Catalyst K from Example 29 was evaluated using similar equipment and the same reaction conditions as Example 3. See Table 17 below.

Table 17

Percent N in Feed Converted to N_2

Temperature, °C	Catalyst K
550	86%
455	97%
400	99%
345	99%
250	92%

Example 31

In this example Catalyst K was hydrothermally treated at 850°C in air containing 20% steam for 6 hours. This catalyst is referred to as Catalyst L.

Example 32

In this example, the SCR activity of the hydrothermally treated catalyst, Catalyst L, from Example 31 was evaluated using similar equipment the same reaction conditions as Example 3. Catalyst activity results are reported below in Table 18.

Table 18

Percent N in Feed Converted to N_2

Temperature, °C	Hydrothermally treated Catalyst L
550	96%
455	99%
400	99%
345	99%
250	96%

Example 33

In this example the hydrothermally treated catalyst, Catalyst L, from Example 31 was aged at 700°C in 100% steam for 7 hours. This catalyst is referred to as Catalyst M.

Example 34

In this example, the SCR activity of the aged, hydrothermally treated catalyst, Catalyst M, from Example 33 was evaluated using similar equipment and the same reaction conditions as Example 3. Catalyst activity results are reported below in Table 19.

Table 19

Percent N in Feed Converted to N_2

Temperature, °C	Aged Catalyst of Example 33
550	99%
455	96%
400	95%
345	93%
250	82%

Example 35

In this example the aged, hydrothermally treated catalyst, Catalyst M, from Example 33 was further aged at 900°C in 100% steam for 7 hours. This catalyst is referred to as Catalyst N.

Example 36

In this example, the SCR activity of the aged, hydrothermally treated catalyst, Catalyst N, from Example 35 was evaluated using similar equipment and the same reaction conditions as Example 3. Catalyst activity results are reported below in Table 20.

Table 20

Percent N in Feed Converted to N_2

Temperature, °C	Aged Catalyst of Example 35
550	86%
455	71%
400	53%
345	28%
250	11%

Example 37

In this example Catalyst K was aged at 700°C in 100% steam for 7 hours without the intermediate hydrothermal treatment. This catalyst will be referred to as Catalyst O.

Example 38

In this example, the SCR activity of the aged catalyst, Catalyst O from Example 37 was evaluated using similar equipment and the same reaction conditions as Example 3. Catalyst activity results are reported below in Table 21.

Table 21

Percent N in Feed Converted to N_2

Temperature, °C	Aged Catalyst of Example 37
550	98%
455	98%
400	97%
345	99%
250	77%

Example 39

In this example the aged catalyst, Catalyst O, from Example 37 was further aged at 900°C in 100% steam for 7 hours. This catalyst will be referred to as Catalyst P.

Example 40

In this example, the SCR activity of the twice-aged catalyst, Catalyst P, from Example 39 was evaluated using similar equipment and the same reaction conditions as Example 3. Catalyst activity results are reported below in Table 22.

Table 22

Percent N in Feed Converted to N_2

Temperature, °C	Aged Catalyst of Example 39
550	56%
455	32%
400	21%
345	14%
250	8%

Example 41

A ZSM-5 catalyst was prepared by the following method: 99 grams of calcined ZSM-5 were mixed in a muller with 20 grams of Dow Corning Q6-2230 silicone resin, and 6.5 grams of Dow Chemical Co. K75M Methocel™. To this dry blend, 52.9 grams of distilled water and 23.1 grams of E. I. DuPont de Nemours & Co. DBE (dibasic ester) were added while mulling. The mixture was then extruded to form 1/16 inch cylindrical extrudates. The extrudates were dried overnight at 120°C and then calcined at 600°C in 10% steam for 10 hours to produce a ZSM-5 containing catalyst. This catalyst is referred to herein as Catalyst Q.

Example 42

An iron containing ZSM-5 sample was prepared by the following method: 99 grams of calcined ZSM-5 were mixed in a muller with 20 grams of Dow Corning Q6-2230 silicone resin, 6.5 grams of Dow K75M Methocel™, and 3.2 grams of iron oxide, Fe_2O_3. To this dry blend, 52.9 grams of distilled water and 23.1 grams of DuPont DBE (dibasic ester) were added while mulling. The mixture was then formed into 1/16 inch cylindrical extrudates. The extrudates were dried overnight at 120°C and then calcined at 600°C in 10% steam for 10 hours to produce an iron containing catalyst, Catalyst R.

Example 43

In this example, the SCR activity of Catalyst Q is compared with the SCR activity of Catalyst R. The catalyst samples were evaluated using a fixed-bed quartz reactor operating between 250 and 550°C. The reactor was loaded with 2.75 grams of catalyst with inlet gases consisting of 500 ppm NO, 500 ppm NH_3, and 5% O_2 in a N_2 carrier flowing at a constant flow rate of 1,000 cc/min. The effluent from

the reactor was continuously monitored by FTIR (Fourier Transform Infrared) analysis. Catalyst activity results are summarized below in Table 23.

Table 23

Net NO Conversion, %

Temperature, °C	Catalyst Q	Catalyst R
550	71%	92%
454	74%	96%
398	72%	96%
343	60%	96%
250	25%	65%

Example 44

An iron containing ZSM-5 sample was prepared by the following method: 99 grams of calcined ZSM-5 were mixed in a muller with 20 grams of Dow Corning Q6-2230 silicone resin, 6.5 grams of Dow K75M Methocel™, and 0.32 grams of iron oxide, Fe_2O_3. To this dry blend, 52.9 grams of distilled water and 23.1 grams of DuPont DBE (dibasic ester) were added while mulling. The mixture was then formed into 1/16 inch cylindrical extrudates. The extrudates were dried overnight at 120°C and then calcined at 600°C in 10% steam for 10 hours to produce an iron containing catalyst, Catalyst S.

Example 45

In this example, the SCR activity of Catalyst Q is compared with the SCR activity of Catalyst S. The catalyst samples were evaluated using a fixed-bed quartz reactor operating between 250 and 550°C. The reactor was loaded with 2.75 grams of catalyst with inlet gases consisting of

500 ppm NO, 500 ppm NH_3, and 5% O_2 in a N_2 carrier flowing at a constant flow rate of 1,000 cc/min. The effluent from the reactor was continuously monitored by FTIR (Fourier Transform Infrared) analysis. Catalyst activity results are summarized below in Table 24.

Table 24

Net NO Conversion, %

Temperature, °C	Catalyst Q	Catalyst S
550	71%	84%
454	74%	86%
398	72%	87%
343	60%	82%
250	25%	40%

Example 46

A component of the in-situ grown ZSM-5 clay aggregate catalyst precursor was prepared by mixing 140 grams of calcined ZSM-5 seeds with 1860 grams of kaolin clay (Kaopaque 10S, a Georgia kaolin clay, Dry Branch Chemical Co., Dry Branch, GA). The mixed components will be referred to herein as Component A.

Example 47

An in-situ grown ZSM-5 clay aggregate catalyst precursor was prepared by mixing 75.9 grams of Component A from Example 46 with 7.6 grams of Dow Chemical Co. K75M Methocel™ in a muller. To this dry blend, 60.3 grams of E. I. DuPont de Nemours & Co. Ludox™ AS-40 colloidal silica were added while mulling. The mixture was then extruded into 1/16 inch cylindrical extrudates. The extrudates were dried overnight at 120°C and then calcined at 1010°C for 3 hours to produce an in-situ grown ZSM-5 catalyst precursor, Precursor A.

Example 48

An iron containing in-situ grown ZSM-5 clay aggregate catalyst precursor was prepared by mixing 75.9 grams of Component A from Example 46 with 7.6 grams of Dow K75M Methocel™ and 3.6 grams of Fe_2O_3 in a muller. To this dry blend, 60.3 grams of DuPont Ludox™ AS-40 colloidal silica were added while mulling. The mixture was then extruded into 1/16 inch cylindrical extrudates. The extrudates were dried overnight at 120°C and then calcined at 1010°C for 3 hours to produce an in-situ grown ZSM-5 catalyst precursor, Precursor B.

Example 49

An in-situ grown ZSM-5 catalyst was prepared by the following method: 100 grams of Precursor A from Example 47 were placed in the bottom of a 1 liter autoclave with 384 grams of water, 16.1 grams of a 50% NaOH solution, and 5.9 grams of n-propylamine. Crystallization was completed under autogenous pressure at 149°C for 6 hours with no additional nutrients. After synthesis, the extrudates were cooled to room temperature, washed and dried at 120°C. The extrudates were NH_4^+ exchanged three times. A hybrid calcination followed which consisted of three hours in nitrogen at 482°C, with air slowly bled in to minimize the exotherm, then the temperature was raised to 537°C and held for six hours to produce an in-situ grown ZSM-5 catalyst, Catalyst T (greater than about 30% crystallinity).

Example 50

An in-situ grown iron-containing ZSM-5 catalyst that should be effective in the method of this invention may be prepared by the following method: about 100 grams of Precursor B from Example 48 may be placed in the bottom of a 1 liter autoclave with about 384 grams of water, about 16.1 grams of a 50% NaOH solution, and about 5.9 grams of n-propylamine. Crystallization should be possible by treating the mixture under autogenous pressure at about

149°C for about 6 hours with no additional nutrients. After synthesis, the extrudates may be cooled to room temperature, and then may be washed and may be dried at 120°C. The extrudates should be NH_4^+ exchanged three times. The ammonium exchanged extrudates may be hybrid calcined, by treating them for about three hours in nitrogen at about 482°C, and then by slowly bleeding air in to minimize the exotherm that may be developed, then raising the temperature to 537°C and holding the extrudates at that temperature for about six hours.

CLAIMS:

1. A catalyst that is useful for treating an exhaust gas comprising NO_x and ammonia, the catalyst comprising an intermediate pore size zeolite and iron or an iron compound that has been hydrothermally treated, the hydrothermal treatment and the iron concentration being effective to produce a catalyst that is capable of converting at least 75 percent of the NO_x and ammonia present in the exhaust gas after the catalyst has been treated in 100 percent steam at a temperature of 700°C for 10 hours.

2. The catalyst of claim 1, wherein the catalyst is bound with silica, zirconia, titania, and combinations thereof.

3. The catalyst of claims 1 and 2, wherein the catalyst has been prepared by the impregnation of the intermediate pore size zeolite with ferrocene in a solvent.

4. The catalyst of claims 1 and 2, wherein the catalyst has been prepared by ion-exchanging iron in an aqueous solution onto the intermediate pore size zeolite under conditions effective to allow the iron to enter the pores of the zeolite. the ion-exchange conditions being further effective to maintain the iron in solution during the ion-exchange treatment, the conditions still further being effective to mantain the iron at a valence of 2 during the ion-exchange treatment.

5. The catalyst of claims 1 and 2, wherein the catalyst has been prepared by contacting the intermediate pore size zeolite with an iron salt or salt precursor in a suitable solvent for the salt or salt precursor.



6. The catalyst of claim 2, wherein the catalyst has been prepared by preparing a physical mixture of dry intermediate pore size zeolite, binder, and iron oxide and then forming the physical mixture into the desired shape.

7. The catalyst of claim 2, wherein the catalyst has been prepared by combining ZSM-5 seeds, silica, clay, and iron oxide into an aggregate; calcining the aggregate at a temperature of at least 1000°C; and crystallizing zeolite in the aggregate by heating the calcined aggregate to a temperature greater than 135°C (275°F) in the presence of caustic, and optionally, at least one organic directing agent.

8. The catalyst of claims 1 through 7, wherein the catalyst has been hydrothermally treated in an atmosphere of up to 100 percent steam at a temperature of from 400°C to 850°C.

9. A process for treating exhaust gas comprising NO_x and ammonia comprising contacting the exhaust gas with the catalyst of claims 1 through 8 under conditions effective for the conversion of at least a portion of the NO_x and ammonia to innocuous compounds.

10. The process of claim 9, wherein the contacting conditions comprise a temperature of from 200°C to 600°C, a pressure of from 34.5 to 3450 kPaa, and at a gas hourly space velocity (GHSV) of 1,000 to 100,000 hr^{-1}.