

Description

All fossil fuel combustion processes generate nitrogen oxides (NOx). The probability that these NOx emissions contribute to the "acid rain" problem, coupled with increased public awareness, prompted the search for catalytic materials which reduce NOx atmospheric emissions.

U.S. Patents 4,220,632 and 3,895,094 disclose the use of zeolites in the selective catalytic reduction of ammonia or other reducing agent. U.S. Patent 4,085,193 teaches the use of titania in the presence of vanadia and other metal oxides for the same purpose. U.S. Patent 4,473,535 teaches copper exchanged zeolite (mordenite) for the same purpose. Many other patents have issued in recent years teaching the reduction of NOx content of exhaust gases. Many NOx containing streams also contain sulfur oxides (SOx) which can adversely affect SCR catalyst performance. It is highly desirable that an SCR catalyst be resistant to poisoning by SOx. The present invention relates to an improved catalyst for the selective catalytic reduction (SCR) of oxides of nitrogen in the presence of a reducing gas such as ammonia in exhaust gas streams, especially those containing SOx.

We have discovered that an NOx selective catalytic reduction catalyst of improved efficiency and stability to poisoning by SOx can be produced by the combination of high surface area zirconia with a natural or synthetic zeolite. The materials are mixed, formed, dried, and fired into a desired shape such as rings or honeycombs, with or without the addition of a ceramic bonding material. The firing takes place at a temperature below the stability limit of the zeolite to form a monolithic body. The zirconia starting material should have a surface area (as measured by the B.E.T. method) of at least 10 square meters per gram, and preferably greater than 50 square meters per gram. A suitable source for the zirconia powder is the hydrololysis product of a zirconium salt.

The preferred amount of zirconia in the product is 10 to 30%, by weight. The operative range of zirconia is from 5 to 50% depending upon other factors. The zeolite should be present in the amount of 50 to 90%. Bond may be present, 0 to 30%.

The catalyst can be further enhanced by the addition of small amounts of promoter in the form of precursors of vanadium oxide and/or copper oxide and/or other base metal oxides. For best stability in the presence of SO₂ the vanadium addition is preferred.

A preferred zeolite is natural clinoptilolite which may be mixed with other zeolites such as chabazite. The zeolite must be primarily in the acid form or thermally convertible to the acid form in the catalytic product. This form may be produced directly by acid exchange or indirectly by ammonium exchange followed by heating to drive off ammonia and convert the material to the hydrogen form.

Zeolites which are useful in this invention are those which can be produced in the hydrogen form by either method and which are stable when in the hydrogen form. Certain zeolites such as zeolite A and sodalite are not stable in the acid form and are not effective in this invention. Examples of zeolites which can be prepared by ammonia and/or acid exchange are mordenite, clinoptilolite, erionite, heulandite, and ferrierite. Zeolites which can be prepared better or only by the ammonium exchange route are natural faujasite and its synthetic counterpart zeolite Y, chabazite and gmelinite.

Mixtures of zeolites may also be used. Other hydrogen form zeolites, such as those of the ZSM series, are prepared by the thermal decomposition of organic templates and are also suitable for use in the catalytic compositions of this invention.

In use the exhaust gas, containing a suitable reducing gas such as ammonia, is passed over the catalyst. Depending upon the requirements of the particular application, the catalyst may be in the form of honeycombs, stacked and arranged, if plural, to provide a through flow path for the gases. Or it may be in the form of randomly dumped saddles, rings, stars, cross partition rings, spheres, pellets, or aggregates or the active catalyst composition can be coated onto a suitable substrate such as cordierite or other ceramic or metal honeycombs. The treated flue gas should be at least 200°C. to prevent deposition of ammonium salts, and may be as high as 650°C. The space velocity is not critical. Typically at 10,000 hourly space velocity (gas volume calculated to standard temperature and pressure) a 1600 ppm NOx content can be reduced by over 90% at 350°C.

Example - Catalyst Preparation.

A composition for making nominal 6 mm (1/4 inch) rings with 3 (1/8 inch) holes was prepared by mixing dry powders consisting of 4,000 grams of a powdered ammonium form of clinoptilolite with 1050 gms of chemically precipitated zirconium dioxide powder having a surface area of about 90 square meters per gram. Water was added in the amount of 1800 ml and mixing was continued for ten minutes.

Concentrated nitric acid, 106 ml, is added and the mixing continued for another ten minutes. Additional water may be added to adjust the consistency of the mix. When the mix is to be extruded 0.2% of an organic cationic polymer extrusion aid may be added after the mix is wet.

After extrusion the rings are dried in an air atmosphere for one to two hours at 200°F. The final firing takes place at 1,000°F. for five hours.

When it is desired to incorporate vanadium or copper into the composition the promoter precursor may be added during the mixing operation, or may be impregnated into the formed product after firing. The added promoter should be present in an amount of at least 0.1% by elemental weight, as the oxide (V_2O_5 or CuO).

Various products were made according to the methods of the Example.

Table I shows the composition of a variety of catalysts made as described above, with varying amounts of zeolite, zirconia, binder and promoter.

The SO_2 concentrations were varied with time. The catalysts initial NO_x reduction activity without SO_2 in the stream was measured over a 24 hour period and is listed in Table II, column 2. Then, 50 ppm SO_2 was added to the stream and the NO_x reduction efficiency measured after an additional 24 hours with the results shown in column 3. Then, this SO_2 concentration was increased to 1600 ppm and the NO_x reduction efficiency measured at 24, 48, and 330 hours, and shown in columns 4, 5, and 6, respectively. Test conditions were :

Temperature, C	350
Oxygen Concentration, Vol %	5
NO_x Concentration, volume parts per million	500
NH_3/NO_x , Vol	1
H_2O	15
N_2	Balance
SO_2	As Indicated

The data of Table II clearly demonstrate that the zirconia containing catalyst of this invention, Sample Number 65411, out-performs the control catalyst, Sample Number 65233. The zirconia containing catalyst not only has a higher initial activity in the absence of SO_2 but, more importantly, remains more active even in the presence of 1600 ppm SO_2 .

TABLE I
SELECTIVE CATALYTIC REDUCTION
CATALYST COMPOSITIONS

<u>Sample Number</u>	<u>Zeolite</u>	<u>ZrO₂</u>	<u>Binder</u>
65233*	90	0	10
65426	0	100	0
65411	80	20	0
*Control			

TABLE II
NOx REMOVAL EFFICIENCIES
OF SELECTIVE CATALYTIC REDUCTION CATALYSTS
BEFORE AND AFTER EXPOSURE TO SO2

Sample Number	Initial Nox Removed	%NOx Removal After 50 ppm SO2 Exposure 24 hours	NOx removal After 1600 ppm SO2 Exposure		
			24 Hrs	48 Hrs	330 Hrs
65233*	72.1	63.9	57.4	47.4	-
65426	9.1	18.2	-	-	-
65411	96.0	84.0	82.0	82.0	81.7

*Control

Claims

1. A catalyst for the selective reduction of NOx to nitrogen in the presence of ammonia, characterized by the fact that said catalyst is a shaped coformed mixture of 5 to 50% by weight of zirconia starting material having a surface area of at least 10 square meters per gram and containing 50% to 90% of one or more zeolites in the hydrogen or ammonium form and 0 to 30% of a bonding agent.

2. A catalyst according to claim 1, characterized by the fact that said zeolite contains a major portion of clinoptilolite.

3. A catalyst according to claim 1, characterized by the fact that said zeolite is clinoptilolite.

4. A catalyst according to claim 1, characterized by the fact that the zirconia is derived from the hydrolysis of a zirconyl salt.

5. A catalyst according to any one of the preceding claims, characterized by the fact that said zirconia is derived from the hydrolysis of one or more zirconium salts to ZrO₂.

6. A catalyst according to any one of the preceding claims, characterized by containing at least 0.1% by weight of a promoter which is an oxide of vanadium or of copper.

7. A catalyst according to any one of the preceding claims, characterized by the fact that the active catalyst composition is coated onto a metal or ceramic support.

8. A catalyst according to any one of the preceding claims, characterized by the fact that the zirconia starting material has a surface area of at least 50 square meter per gram.

9. A catalyst according to any one of the preceding claims, characterized by being in the form of rings, spheres, cross partition rings, stars, saddles, aggregates, honeycombs, or pellets.

Patentansprüche

1. Katalysator für die selektive Reduktion von NOx zu Stickstoff in Anwesenheit von Ammoniak, dadurch gekennzeichnet, daß der Katalysator eine gestaltete, gemeinsam geformte Mischung von 5 bis 50 Gew.-% Zirkonoxid-Ausgangsmaterial mit einer spezifischen Oberfläche von zumindest 10 m²/g und einem Gehalt von 50 bis 90 % an einem oder mehreren Zeolithen in der Wasserstoff- oder Ammoniumform und 0 bis 30 % an Bindemittel ist.

2. Katalysator gemäß Anspruch 1, dadurch gekennzeichnet, daß der Zeolith einen überwiegenden Anteil Klinoptilolith enthält.

3. Katalysator gemäß Anspruch 1, dadurch gekennzeichnet, daß der Zeolith Klinoptilolith ist.

4. Katalysator gemäß Anspruch 1, dadurch gekennzeichnet, daß das Zirkonoxid der Hydrolyse eines Zirkonysalzes entstammt.

5. Katalysator gemäß einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Zirkonoxid der Hydrolyse eines oder mehrerer Zirkoniumsalze unter Bildung von ZrO₂ entstammt.

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6. A catalyst according to any one of the preceding claims, characterized by containing at least 0.1% by weight of a promoter which is an oxide of vanadium or of copper.
7. A catalyst according to any one of the preceding claims, characterized by the fact that the active catalyst composition is coated onto a metal or ceramic support.
8. A catalyst according to any one of the preceding claims, characterized by the fact that the zirconia starting material has a surface area of at least 50 square meter per gram.
9. A catalyst according to any one of the preceding claims, characterized by being in the form of rings, spheres, cross partition rings, stars, saddles, aggregates, honeycombs, or pellets.

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1. Katalysator für die selektive Reduktion von NO_x zu Stickstoff in Anwesenheit von Ammoniak, dadurch gekennzeichnet, daß der Katalysator eine gestaltete, gemeinsam geformte Mischung von 5 bis 50 Gew.-% Zirkonoxid-Ausgangsmaterial mit einer spezifischen Oberfläche von zumindest 10 m²/g und einem Gehalt von 50 bis 90 % an einem oder mehreren Zeolithen in der Wasserstoff- oder Ammoniumform und 0 bis 30 % an Bindemittel ist.
2. Katalysator gemäß Anspruch 1, dadurch gekennzeichnet, daß der Zeolith einen überwiegenden Anteil Klinoptilolith enthält.
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4. Katalysator gemäß Anspruch 1, dadurch gekennzeichnet, daß das Zirkonoxid der Hydrolyse eines Zirkonylsalzes entstammt.
5. Katalysator gemäß einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Zirkonoxid der Hydrolyse eines oder mehrerer Zirkoniumsalze unter Bildung von ZrO₂ entstammt.
6. Katalysator gemäß einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß er zumindest



0,1 Gew.-% eines Promotors enthält, bei dem es sich um ein Oxid des Vanadins oder Kupfers handelt.

7. Katalysator gemäß einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die aktive katalysatorzusammensetzung als Überzug auf einen metallischen oder keramischen Träger aufgebracht wird.

8. Katalysator gemäß einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Zirkonoxid-Ausgangsmaterial eine spezifische Oberfläche von zumindest 50 m²/g besitzt.

9. Katalysator gemäß einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß er in Form von Ringen, Kugeln, Ringen mit Quertellung, Sternen, Sätteln, Aggregaten, Waben oder Pellets vorliegt.

Revendications

1. Un catalyseur pour la réduction sélective de NO_x en azote en présence d'ammoniac, caractérisé par le fait que ledit catalyseur est un mélange co-formé mis en forme de 5 à 50 % en poids d'une matière de départ à base de zircone, présentant une surface spécifique d'au moins 10 m² par gramme et renfermant de 50 % à 90 % d'une ou de plus d'une zéolite sous la forme hydrogène ou ammonium et de 0 à 30 % d'un agent liant.

2. Un catalyseur selon la revendication 1, caractérisé par le fait que ladite zéolite renferme une proportion principale de clinoptilolite.

3. Un catalyseur selon la revendication 1, caractérisé par le fait que ladite zéolite est la clinoptilolite.

4. Un catalyseur selon la revendication 1, caractérisé par le fait que la zircone est dérivée de l'hydrolyse d'un sel de zirconyle.

5. Un catalyseur selon l'une quelconque des revendications précédentes, caractérisé par le fait que ladite zircone est dérivée de l'hydrolyse d'un ou de plus d'un sel de zirconium en ZrO₂.

6. Un catalyseur selon l'une quelconque des revendications précédentes, caractérisé par le fait qu'il renferme au moins 0,1 % en poids d'un promoteur qui est un oxyde de vanadium ou de cuivre.

7. Un catalyseur selon l'une quelconque des revendications précédentes, caractérisé par le fait que la composition active de catalyseur est appliquée sur un support métallique ou céramique.

8. Un catalyseur selon l'une quelconque des revendications précédentes, caractérisé par le fait que le matériau de départ à base de zircone présente une surface spécifique d'au moins 50 m² par gramme.

9. Un catalyseur selon l'une quelconque des revendications précédentes, caractérisé par le fait qu'il est sous la forme d'anneaux, de sphères, d'anneaux à cloisonnement transversal, d'étoiles, de selles, d'agréats, d'éléments en nids d'abeilles ou de pastilles.

