

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
8 January 2004 (08.01.2004)

PCT

(10) International Publication Number
WO 2004/002611 A1

- (51) International Patent Classification⁷: **B01D 53/86**, 53/94, B01J 29/40, 23/10
- (21) International Application Number: PCT/GB2003/002663
- (22) International Filing Date: 20 June 2003 (20.06.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 0214968.0 28 June 2002 (28.06.2002) GB
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- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 2004/002611 A1

(54) Title: DOPED CERIA-CONTAINING ZEOLITE-BASED NH₃ SCR CATALYST

(57) Abstract: A catalyst for catalysing the selective reduction of NO_x with NH₃ comprises an alumino-silicate zeolite supporting doped ceria. Suitable dopants include zirconium, lanthanum, alumina, yttrium, praseodymium, neodymium or any mixture of two or more thereof. The catalyst can be used for treating gas streams from stationary power sources such as coal or petroleum fired power plants or boilers, gas turbines or a diesel engines.

ZEOLITE-BASED NH₃ SCR CATALYST

5 The present invention relates to a catalyst for selectively reducing NO_x with NH₃, and in particular to a catalyst comprising an alumino-silicate zeolite having relatively higher selectivity at higher temperatures.

10 It is known to remove oxides of nitrogen (NO_x) pollutants from exhaust streams or other gaseous emission sources which contain excess oxygen by adding NH₃ to the gas stream in a proportion based on the amount of NO_x present and reacting the NH₃ and NO_x over a catalyst to form non-polluting N₂ and H₂O.

15 A wide variety of catalysts have been proposed for this purpose. Amongst these, zeolite based catalysts are indicated for higher temperature applications (350-600°C or above). The suitability of zeolite catalysts for SCR above about 450°C has been known since the 1970s, when the zeolite mordenite was identified as an active SCR catalyst. An advantage of zeolites is that when NO_x is present, the catalyst does not oxidise ammonia to NO_x according to the reaction $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$. Therefore, unlike Pt- and V₂O₅-based catalysts, the selectivity of zeolite catalysts toward NO_x conversion
20 continually increases with temperature.

 At exposure temperatures above about 600°C, in a high water content process stream, zeolites tend to deactivate by a process called de-alumination whereby the Al³⁺ in
25 the SiO₂-Al₂O₃ framework migrates out of the structure. This leads to permanent deactivation and, in the extreme case, collapse of the crystalline structure.

 Zeolite structures can be ion-exchanged by other cations while maintaining electrical neutrality, altering the chemistry of catalytically active sites. See, for example,
30 US-A-4,961,917 (the entire contents of which are incorporated herein by reference) which describes a zeolite catalyst composition which comprises a metal (e.g., iron or copper) promoted zeolite, the zeolite being characterised 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
35 about 7 Angstroms. Advantages of this material are described as high tolerance for sulfur

poisoning, good activity for the SCR of NO_x with NH₃, good activity for the oxidation of NH₃ with O₂, and the retention of such good activities even under high temperature operations, e.g. 400°C, or higher, and hydrothermal conditions.

A problem with the zeolite catalyst composition described in US-A-4,961,917 is explained in WO-A-02/41991 wherein under harsh hydrothermal conditions, such as reduction of NO_x from gas turbine exhaust at temperatures exceeding 500°C, the activity of the iron-promoted zeolite begins to decline. This decline in activity is believed to be due to destabilisation of the zeolite such as by dealumination and consequent reduction of metal-containing catalytic sites within the zeolite.

WO-A-02/41991 (the entire contents of which are incorporated herein by reference) describes an improvement over the catalyst of US-A-4,961,917 in that the zeolite is a metal-promoted beta zeolite in which the zeolite is pre-treated so as to provide it with improved hydrothermal stability. The stabilised beta zeolite is provided by incorporating into the zeolite structure no-framework aluminium oxide chains.

In our WO-A-99/55446 (the entire contents of which are incorporated herein by reference) we describe a zeolite-based SCR catalyst, such as ZSM-5, which desirably can contain from 1-10 wt% of metal e.g. copper, cerium, iron or platinum in order to improve low temperature SCR activity.

EP 0 299 294 describes a ferro-silicate zeolite for catalysing the selective reduction of nitrogen oxides from oxygen-containing exhaust gases with ammonia.

We have now devised a zeolite-based catalyst which has improved selectivity for high temperature NH₃ SCR of NO_x over prior art catalysts. Such improvement is retained following high temperature lean hydrothermal ageing of the catalyst.

According to one aspect, the invention provides a catalyst for catalysing the selective reduction of NO_x with NH₃, which catalyst comprising an alumino-silicate zeolite supporting doped ceria.

An advantage of the catalysts of the present invention over prior art catalysts, such as iron beta zeolites, is that the activity of the iron beta zeolite catalysts is more significantly inhibited by the presence of hydrocarbon in the exhaust gas. We have also found that the catalysts of the present invention are particularly applicable when used to treat exhaust gases resulting from the combustion of low sulfur fuels such as MK1.

The ceria dopant can be any suitable element, but is typically a metal or metal oxide such as zirconium, lanthanum, alumina, yttrium, praseodymium, neodymium or any mixture of two or more thereof. Preferably, the ceria dopant is zirconium.

Together, the ceria and the dopant can be present in an amount comprising from about 0.1 to about 20 wt% of the catalyst, such as from about 5 to about 15 wt%, and preferably about 10 wt%. It will be appreciated, however, that in certain embodiments of the invention high wt% of ceria and dopant together may promote undesirable non-selective oxidation of NH_3 .

The weight ratio of ceria to dopant can be from about 1:5 to about 5:1, such as about 1:3 to about 3:1, preferably about 1:1.

Without wishing to be bound by theory, we believe that the ceria and the or each dopant can be present in the catalyst as a mixture of each material, as a mixed oxide including ceria and at least one dopant or any mixture of two or more thereof.

In a preferred embodiment, at least some of the ceria and/or the dopant is present as an oxysulfur compound. Methods for producing such oxysulfur compounds are known to the person skilled in the art and include contacting the zeolite with sulfuric acid, impregnation of the zeolite material with a sulfate-containing metal precursor e.g. $\text{Ce}(\text{SO}_4)_2$ (aq) (see US-A-4,780,445, the entire contents of which are incorporated herein by reference) or by lean hydrothermal sulfur ageing.

The catalyst can be any suitable alumino-silicate zeolite material for the purpose. Typical zeolites which can be used, with advantage, in the present invention include

ZSM-5, ZSM-8, ZSM-11, ZSM-12, ZSM-20, mordenite, gamma-zeolite, beta-zeolite, silicalite, X zeolite, Y zeolite, L zeolite, erionite, USY zeolite or any mixture of two or
5 more thereof. The zeolite can be dealuminised by methods known in the art to increase the silica to alumina ratio if desired. One such method is described in WO-A-02/41991 and involves the pre-steaming of the zeolite material prior to the inclusion of the ceria and dopant. The conditions can be 600 to 800°C, preferably 650-750°C for 0.25 to 8 hours, preferably 0.5 to 4 hours and most preferably 1 to 2 hours.

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According to a further aspect, the invention provides a substrate comprising a catalyst according to the invention. Depending on the application, the substrate can be a monolith comprised of a refractory material such as a ceramic e.g. cordierite, or a metal such as FecralloyTM or stainless steel. The arrangement of the monolith can be a
15 honeycomb, a tube, a sheet, e.g. stainless steel plates arranged in parallel, or a mesh, particularly a wire mesh. Alternatively, the zeolite can be used as a component in a substrate composition, e.g. including SiC, and extruded into pellets or formed into a monolith structure. Honeycomb cell densities vary, depending on their use. The flow rate of the gas stream can depend on the catalyst volume. Typical flow rates in specific
20 applications include about 3,000 to 5,000 l hr⁻¹ in high dust coal/petroleum-fired power plants having cell densities of from 9-11 cells per square inch (cpsi), 5,000 to 10,000 l hr⁻¹ in low dust coal/petroleum-fired power plants using 11-50 cpsi honeycomb monoliths and 20,000 to 40,000 l hr⁻¹ using 200 cpsi in gas turbines. Diesel engine applications can use 200-600 cpsi monoliths, e.g. a 400 cpsi configuration.

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According to a further aspect, the invention provides a stationary power source comprising a catalyst according to the invention. The stationary power source can be a coal or petroleum fired power plant or boiler, a gas turbine or a diesel engine.

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According to a further aspect, the invention provides a mobile power source comprising a catalyst according to the invention. The mobile power source can also be a diesel engine, and it can provide the propulsive force for a vehicle, such as a passenger vehicle, van or truck, for example.

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According to a further aspect, the invention provides the use of a catalyst according to the present invention for reducing NO_x in a gas stream using NH_3 . The temperature of the gas stream in such use can be from about 350 to about 600°C, but is preferably in the range of from about 450 to about 550°C.

Methods of manufacture of catalysts and catalyst coated substrates according to the invention are known to the person skilled in the art and no detailed explanation will be given here. Generally, such methods can include co-precipitation or wet impregnation of bulk zeolite with an aqueous solution including a mixture of ceria and the or each dopant salt, followed by drying and calcining the resulting material. In an alternative wet impregnation method, the zeolite support can be impregnated sequentially, first with an aqueous solution of the ceria salt or the or each dopant salt, followed by the drying and the calcining step, and the resulting material can then be impregnated with an aqueous solution of the or each dopant salt or the ceria salt. However the zeolite material is obtained, it is then made up into a washcoat and coated on the chosen substrate to obtain the desired loading.

Alternatively, a zeolite-containing washcoat can be prepared and coated on a suitable substrate, followed by a drying and calcining step. The resulting coated substrate can then be wet impregnated with an aqueous solution including salts of the or each dopant and ceria, or a sequential application similar to the method outlined above.

In order that the invention may be more fully understood, the following Example is provided by way of illustration only and with reference to the accompanying drawing, in which:

Figure 1 is a graph showing NO_x conversion against temperature for a fresh and aged catalyst comprising Ce-Zr/ZSM-5 according to the invention and a fresh and aged catalyst comprising Ce/ZSM-5 for the purposes of comparison.

EXAMPLE

A catalyst according to the invention was prepared by wet impregnation of cerium nitrate and zirconium nitrate on bulk ZSM-5. The resulting material was dried

at 110°C for 24 hrs and calcined at 500°C for 2 hrs. The resulting catalyst material contained about 10wt% ceria and zirconia and the weight ratio of ceria to zirconia was approximately 1:1.

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A comparative catalyst was prepared in a similar manner to include 5wt% ceria and no dopant.

10 A sample of each catalyst powder was subjected to lean hydrothermal ageing at 600°C in air/10% H₂O for 337 hrs.

Fresh and aged powder samples of each catalyst were tested in a laboratory reactor in a synthetic gas mixture designed to mimic the composition of a diesel exhaust gas. The synthetic gas composition used was: 200ppm NO, 200ppm NH₃, 12% O₂, 4.5% H₂O, 4.5% CO₂, 200ppm CO, 100ppm C₃H₆, 20ppm SO₂, balance N₂. The reactor temperature was ramped at a rate of 5°C per minute and the NO_x conversion downstream of catalyst sample was detected and plotted against temperature. The results are shown in Figure 1.

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As can be seen, the fresh Ce-Zr/ZSM-5 catalyst according to the invention shows an increased selectivity for the selective reduction of NO_x with NH₃ at temperatures above about 400°C compared with the Ce/ZSM-5 catalyst (without the dopant).

The improvement is more marked when the aged catalysts are compared. 25 The peak NO_x conversion of the aged catalyst according to the invention is approximately 20% higher than the comparative catalyst and 20% greater NO_x conversion at 550°C. Light-off temperature (the temperature at which a catalyst catalyses a reaction at 50% efficiency) is shifted up 80°C for both catalysts following lean hydrothermal ageing, yet the catalyst according to the invention catalyses peak, or within 30 10°C of peak, NO_x conversion above 430°C in the important high temperature range of 400-600°C. Thus the present invention provides considerable advantages over the prior art comparative catalyst.

CLAIMS:

1. A catalyst for catalysing the selective reduction of NO_x with NH₃, which catalyst
5 comprising an alumino-silicate zeolite supporting doped ceria.
2. A catalyst according to claim 1, wherein the ceria dopant is zirconium,
lanthanum, alumina, yttrium, praseodymium, neodymium or any mixture of two or more
thereof.
- 10 3. A catalyst according to claim 1, wherein the ceria dopant is zirconium.
4. A catalyst according to claim 1, 2 or 3, wherein the ceria and dopant comprise
from 0.1 to 20 wt% of the catalyst.
- 15 5. A catalyst according to claim 4, wherein the ceria and dopant comprise from 5 to
15 wt% of the catalyst.
6. A catalyst according to claim 4 or 5, wherein the ceria and dopant comprise
20 10 wt% of the catalyst.
7. A catalyst according to any of claims 1 or 6, wherein the weight ratio of ceria to
dopant is 1:5 to 5:1.
- 25 8. A catalyst according to claim 7, wherein the weight ratio of ceria to dopant is 1:3
to 3:1.
9. A catalyst according to claim 7 or 8, wherein the weight ratio of ceria to dopant
is 1:1.
- 30 10. A catalyst according to any preceding claim, wherein at least some of the ceria
and/or the dopant is present as an oxysulfur compound.
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11. A catalyst according to any preceding claim, wherein the zeolite is ZSM-5, ZSM-8, ZSM-11, ZSM-12, ZSM-20, mordenite, gamma-zeolite, beta-zeolite, silicalite, X, zeolite, Y zeolite, L zeolite, erionite, USY zeolite or any mixture of two or more thereof.
12. A catalyst according to any of claims 1 to 10, wherein the zeolite is ZSM-5.
- 10 13. A catalyst according to claim 11 or 12, wherein the zeolite is dealuminised.
14. A substrate comprising a catalyst according to any preceding claim.
15. A stationary power source comprising a catalyst according to any of claims 1 to 13.
- 15 16. A stationary power source according to claim 15, wherein it is a coal or petroleum fired power plant or boiler, a gas turbine or a diesel engine.
- 20 17. A mobile power source comprising a catalyst according to any of claims 1 to 13.
18. A mobile power source according to claim 17, wherein it is diesel engine.
19. A vehicle including a mobile power source according to claim 17 or 18.
- 25 20. The use of a catalyst according to any of claims 1 to 13 for reducing NO_x in a gas stream using NH₃.
21. The use according to claim 20, wherein the temperature of the gas stream is from 30 350 to 600°C.
22. The use according to claim 21, wherein the temperature of the gas stream is from 450 to 550°C.

23. The use according to claim 20, wherein the gas stream is from a stationary power source.

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24. The use according to claim 23, wherein the stationary power source is a coal or petroleum fired power plant or boiler, a gas turbine or a diesel engine.

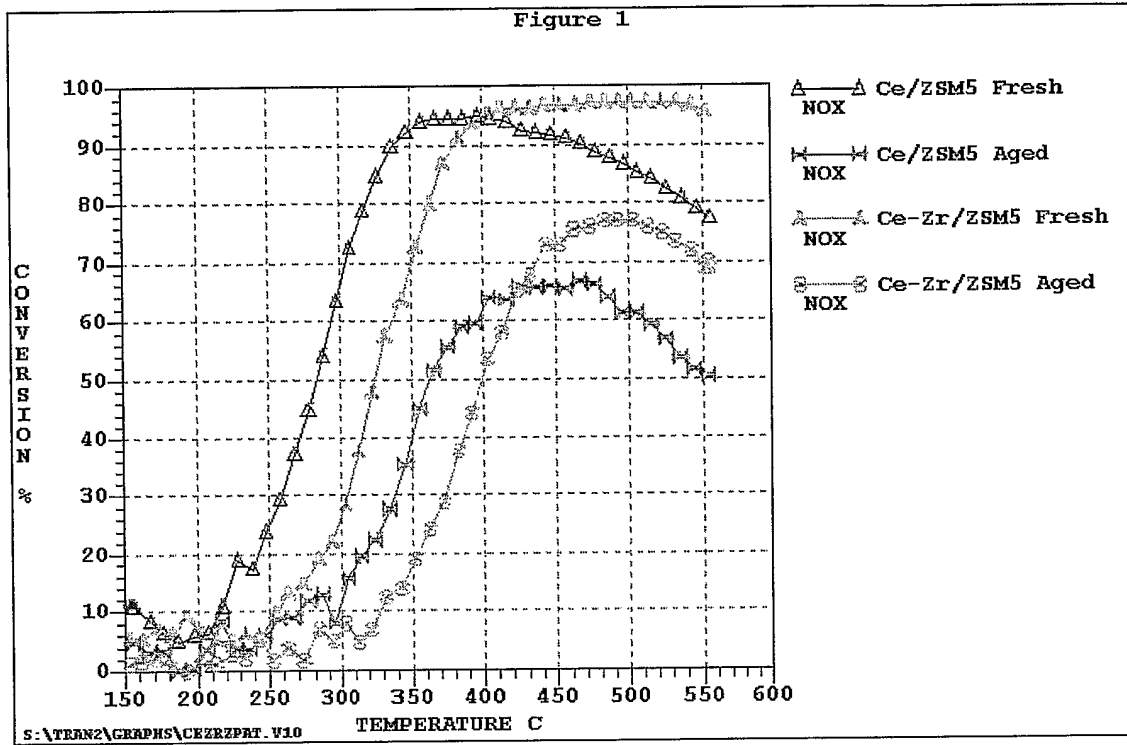
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25. The use according to claim 20, wherein the gas stream is from a mobile power source.

26. The use according to claim 25, wherein the mobile power source is a diesel engine.

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27. The use according to claim 25 or 26, wherein the mobile power source is part of a vehicle.



INTERNATIONAL SEARCH REPORT

Intel | Application No
PCT/GB 03/02663

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/86 B01D53/94 B01J29/40 B01J23/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 6 047 544 A (ETOU SATOMI ET AL) 11 April 2000 (2000-04-11) column 14, line 13-56; claims 1,2,4,6,19 column 15, line 25-33 column 17, line 31-52 --- -/--	1-3,7,8, 11-14, 17,19

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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Date of the actual completion of the international search

24 September 2003

Date of mailing of the international search report

10/10/2003

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INTERNATIONAL SEARCH REPORT

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