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(54) Title: METHOD FOR THE REMOVAL OF NO_X AND CATALYST THEREFOR

(57) Abstract: The invention relates to a method for the catalytic reduction of NO_x in an NO_x containing gas using methane in the presence of a catalyst which comprises a palladium-containing zeolite. In this process one uses a zeolite based on rings of 12 oxygen atoms, wherein the zeolite also comprises scandium, yttrium, a lanthanide or a combination thereof. The invention also relates to the catalyst itself and the preparation thereof.

Method for the removal of NO_x and catalyst therefor

Field of invention

The invention relates to a method for the catalytic reduction of NO_x in an NO_x containing gas using methane in the presence of a catalyst which comprises a palladium-containing zeolite. The invention also relates to a catalyst which comprises a palladium-containing zeolite. The invention also relates to the preparation of this catalyst.

Background of invention

NO_x is released in combustion processes in, for example, gas engines. At present only very few gas engines are equipped with a deNO_x installation. Apart from NO_x, the exhaust gases of gas engines contain considerable amounts of uncombusted methane; sometimes up to 3% of the fuel leaves the engine uncombusted. These methane emissions must also be controlled as part of the reduction of greenhouse gas emissions.

NO_x can also be released from gas burners in horticulture, generating sets, emergency power supplies, gas turbines of (small-scale) combined heat and power systems, and in the industrial production of, for example, cement, nitric acid, iron or caprolactam, in traffic and in the burning of household refuse.

There are various techniques on the market for reducing NO_x emissions, such as low-NO_x burners and selective catalytic reduction with ammonia or urea. These techniques, however, are impossible or expensive to apply for many (small-scale) (gas burner) installations which produce NO_x. There is therefore a demand for an inexpensive downstream technique for the reduction of NO_x.

US Patents 5,149,512 and 5,260,043 describe methods in which NO_x is removed with the aid of methane and in which *inter alia* a catalyst is used which consists of a ZSM-5 zeolite loaded with cobalt. This catalyst, however, only has limited activity for the catalytic reduction of NO_x with methane. In the absence of water, temperatures above 450°C are

necessary for an NO_x removal efficiency above 50%. In the presence of water, however, it must be expected that the NO_x conversion will decrease by about half.

According to the review article by Traa et al., Co-ZSM-5 can also be used for the reduction of NO_x with propane (Y. Traa, B. Burger, J. Weitkamp, Micr. Mes. Mater. **30** (1999) 3-41). It was found here that the method of preparation of the catalyst was critical, and that much higher activities were obtained if the zeolite was loaded with cobalt by the impregnation method (incipient wetness).

A much more efficient catalyst for the reduction of NO_x with methane was found in the form of ZSM-5 with palladium. It is true that these zeolites have a higher activity than zeolites based on cobalt, but it turns out that the activity of the Pd zeolite catalyst also decreases greatly in the presence of water. Loss of activity is also clearly observed as a function of time. (see for example Y. Traa, B. Burger, J. Weitkamp, Micr. Mes. Mater. **30** (1999) 3-41).

Ogura et al. (M. Ogura, S. Kage, M. Hayashi, M. Matsukate and E. Kikuchi, Appl. Catal. B **27** (2000), L213-216) describe the stabilization of Pd-ZSM-5 with the aid of *inter alia* cobalt, rhodium, silver, cerium or iron. It is apparent from this study that cobalt is highly suitable as a stabilizer. Cobalt might also have a promoting effect on the reaction (promotor). The other elements, rhodium, silver, cerium and iron, are promotors in the reaction and also provide Pd-ZSM-5 stabilization.

From Figure 3 in this publication, however, it can be deduced that although these elements can have a stabilizing effect (the half-life increases), it also turns out that the initial conversion activity decreases: if loaded with rhodium the initial activity goes from 49.7% to 18.9% (drop of about 60%), with silver the initial activity goes from 49.7% to 29.9% (drop of about 40%), with cerium the initial activity goes from 49.7% to 39.6% (drop of about 20%) and with iron the initial activity goes from 49.7% to 40% (drop of about 20%). In a number of cases, this may mean that for a substantial part of its life the stabilized catalyst has a lower activity than the non-stabilized catalyst. That is not desirable. The fact that the

initial conversions differ so much with the different metal combinations also makes it almost impossible here to check whether there is in fact any stabilizing effect at all.

Only for the Pd-ZSM-5 catalyst stabilized with cobalt (Figures 1 and 2 of this publication) does it appear to be true that the activity scarcely decreases as a result of the addition of (3.3% by weight) cobalt, while good stabilization is indeed obtained (in any case for a reaction time up to about 14 h). On the basis of this article the person skilled in the art would opt for a Pd-Co-ZSM-5 catalyst for the reduction of NO_x using methane. The activity of this catalyst is limited, however: only 60% NO_x conversion is achieved at 500°C; the stability after about 14 h is not known.

In US Patent 6,063,351 a catalyst based on this palladium-cobalt pairing, with mordenite (MOR) as carrier, is described for the reduction of NO_x with methane. This catalyst has markedly improved activity compared with the cobalt catalyst of the above-mentioned US Patent 5,149,512. Experimentally, however, the stability of this catalyst is found to be inadequate in the long term.

Japanese patent abstracts JP 09 192486, JP 08 164338 and JP 07 32325 also describe catalysts in which Pd may be present. However, none of these abstracts show or indicate that palladium should be present as an ion coordinated by a zeolite. In contrast, for example JP 08 164338 describes that Pd (oxide) layers are present on a zeolite, and JP 07 32325 describes that oxides are present on a γ-alumina substrate. The disadvantages of these catalysts are the same as the disadvantages of the other catalysts know from the art and described above.

Summary of invention

It is therefore the object of this invention to find an efficient method for the catalytic reduction of NO_x in an NO_x containing gas using methane, with the aid of a suitable catalyst. It is furthermore an object of the present invention that this catalytic reduction shall also take place efficiently in the presence of water in the NO_x comprising gas. It is also an

object to find a catalyst with a high activity for the catalytic reduction of NO_x and with a high stability.

Surprisingly it was found that a zeolite based on rings having 12 oxygen atoms also containing palladium ions, with the zeolite also containing scandium, yttrium, a lanthanide or a combination thereof, gives excellent results in the catalytic reduction of NO_x with the aid of methane. In this way an inexpensive NO_x reduction technique is obtained. Methane is relatively cheap and available almost everywhere from the natural gas network. The invention therefore relates to a method for the catalytic reduction of NO_x in an NO_x containing gas using methane in the presence of a catalyst which comprises a palladium-containing zeolite, characterized by using a zeolite based on rings having 12 oxygen atoms, wherein the zeolite also contains scandium, yttrium, a lanthanide or a combination thereof.

The invention also relates to this catalyst, which comprises a palladium-containing zeolite, wherein the palladium in the zeolite is wholly or partially coordinated as ion by the zeolite, wherein the zeolite is based on rings of 12 oxygen atoms, and wherein the zeolite is also loaded with scandium, yttrium or a lanthanide or a combination thereof.

The invention also relates to a method for the preparation of such a catalyst, wherein the zeolite is loaded with scandium, yttrium, a lanthanide or a combination thereof and optionally other metals after having been loaded with palladium by ion exchange.

Description of invention

In the description of the invention NO_x is defined as nitrogen oxides where x (or the O/N ratio) is greater than or equal to 1, such as NO, NO_2, N_2O_3 etc. N_2O, laughing gas, is not included in this definition. NO is usually in equilibrium with other nitrogen oxides, where x is greater than 1, and oxygen

"Methane" or a "methane containing gas" means methane, but can also mean natural gas or another gas mixture containing methane and other gases. "Palladium-containing" means that palladium ions are present in the channels (pores) and/or cages of the zeolite. Lanthanides

(Ln) are the elements 57 (La, lanthanum) to 71 (Lu, lutetium) inclusive. "Metal" or "element" means that the elements can be present as a metal, as a metal compound (notably oxides), but also as an ion of the element/metal.

The NO_x containing gas can for example be the gas released by a gas engine or a gas burner, but can also be an exhaust gas from nitric acid synthesis. The gas can also contain oxygen and/or water. Unlike most catalysts according to the prior art, the catalyst according to the invention loses little or no activity in the presence of water. This is true in particular if the water is present in quantities up to about 5-15%, e.g. 12%. Oxygen can for example be present up to about 20%. The gas may also contain carbon monoxide (CO), that can be removed (partially or completely) by the catalyst of the invention. Hence, the invention is also directed to a method where a catalyst is also used for the removal of NO_x and carbon monoxide, e.g. in exhausts of gas engines. CO may be present in amounts of e.g. 1-2000 ppm or more.

The invention encompasses a method for the catalytic reduction of NO_x in an NO_x containing gas using methane in the presence of a catalyst which comprises a palladium-containing zeolite, characterized by using a zeolite based on rings having 12 oxygen atoms, wherein the zeolite also contains scandium, yttrium, a lanthanide or a combination thereof. The invention is also direct to such catalyst.The palladium is brought into the zeolite by ion exchange, before other (active) metals are introduced into and/or onto the zeolite. The ion exchange step is important, as is also the order of introduction of the metals. Impregnation is generally a simple and cheaper method of putting metals into a carrier, and this method is often used for this reason (among others by Cordoba et al.: L. F. Cordoba, M. Flytzani-Stephanopoulos, C. Montes de Correa, Appl. Catal. B **33** (2001), 25-33).

Cordoba et al. (L. F. Cordoba, M. Flytzani-Stephanopoulos, C. Montes de Correa, Appl. Catal. B **33** (2001), 25-33) choose a method for the reduction of NO_x in which a catalyst is used based on cerium-palladium-mordenite and NO_x is reduced with the aid of dodecane as reducing medium. In this catalyst for this reaction, however, impregnated cerium is the active element and impregnated palladium the promotor.

If the catalyst according to Cordoba et al. is used for the reduction of NO_x with methane, this is found to be inadequate: methane is partially combusted instead of reducing NO_x. If dodecane has to be used, the presence of PdO (present after impregnation and calcination) is favourable for the combustion of coke precursors on the catalyst surface. The presence of PdO is found to be unwanted in the case of methane, however: methane is oxidized and less reaction with NO_x can then take place. The palladium must therefore be brought into the zeolite by ion exchange, so that the palladium ion (especially as Pd^{2+}), wholly or partially coordinated by the zeolite lattice, and not as PdO, is present in the zeolite lattice. For palladium it is surprisingly found that it is important for the method of the present invention that palladium is introduced by ion exchange. Therefore, the zeolite is loaded with scandium, yttrium, a lanthanide or a combination thereof and optionally other metals after having been loaded with palladium by ion exchange.

The expression 'wholly or partially coordinated by the zeolite' means that the palladium has been introduced by ion exchange, and the palladium as ion (Pd^{2+} for example) is exchanged for cations especially in the pores which (via oxygen) are associated with aluminium. The palladium ion is therefore exchanged for at least 1 cation of the zeolite and is thus coordinated by the zeolite. The palladium can also be coordinated by an anion from the solution (which has been used for the exchange), but can also be exchanged with a second cation from the pores. In this way the palladium is then completely coordinated by the zeolite and the palladium is in any case after ion exchange substantially present as an ion and not as palladium oxide. Palladium may have been exchanged with H^+ and NH_4^+, for example. The exchange will take place particularly in the pores. The zeolite is preferably loaded with 0.02 to 2% by weight of palladium. Here, "% by weight" refers to the amount of zeolite exchanged with palladium.

The fact that palladium is present as an ion can also be determined with the aid of IR measurements (FTIR). A non-exchanged zeolite has a lattice vibration band at about 1050 cm^{-1}, whereas a zeolite exchanged with Pd^{2+} has this band at about 950 cm^{-1}. Such a band at about 950 cm^{-1} is also absent after impregnation, which means that Pd is not present as Pd-ions but as PdO, e.g. as PdO clusters. The catalyst of the present invention therefore

comprises a zeolite exchanged with Pd^{2+}, with an absorption signal being found with FTIR at about 950 cm^{-1}, as a result of a zeolite lattice vibration. As described above, this zeolite, based on rings having 12 oxygen atoms, has been or is further loaded with scandium, yttrium or a lanthanide or a combination thereof.

The zeolite for the method for the catalytic reduction of NO_x according to the invention, in which the palladium is introduced by ion exchange, belongs to the group of zeolites which contain 12-rings (12 O atoms). The term "12-ring" means that in the zeolite channels or pores are present which are constructed of rings of Si/Al and oxygen and in which 12 oxygen atoms are present. Surprisingly these zeolites are found to be much more satisfactory for the present method than zeolites based on 10-rings, for example, such as ZSM-5. The zeolite to be used according to the invention therefore comprises a zeolite wherein 12-rings are present, such as, for example, FAU, MOR, BEA, EMT, CON, BOG or ITQ-7, etc., or other zeolites based on 12-rings, which are known to the person skilled in the art, or combinations thereof, e.g. FAU and MOR. The silicon/aluminium ratio is preferably 2 or greater. Particularly good results are achieved when the zeolite is MOR.

Scandium, yttrium and/or one or more lanthanides are put in the zeolite as a stabilizing element. Examples of these elements are lanthanum, cerium, praseodymium, gadolinium, terbium, dysprosium, or combinations such as cerium and gadolinium, etc. The introduction can take place by ion exchange in the liquid phase, but the loading can also be obtained by pore volume impregnation (incipient wetness technique). Hence, the invention also comprises a method where the zeolite is loaded with scandium, yttrium, a lanthanide or a combination thereof by ion exchange or incipient wetness techniques. It is important that this step takes place after the introduction of the palladium ion. Surprisingly it is found that this combination of (a) a Pd zeolite based on rings having 12 oxygen atoms, where (b) the zeolite also contains scandium, yttrium, a lanthanide or a combination thereof, gives excellent results in the present method for the catalytic reduction of NO_x in an NO_x containing gas using methane. The second element increases the stability and preferably furthermore increases the initial activity, even in the presence of water.

In another embodiment, the zeolite is loaded with scandium, yttrium, a lanthanide or a combination thereof by physically mixing the zeolite with salts or oxides of said metals. Also this method to obtain the catalyst provides good results for the method of the invention for the catalytic reduction of NO_x with methane. Here, the term 'loaded' is used to indicate that the zeolite is physically mixed with salts or oxides of said metals (or combinations thereof). Mixing will mainly be done by dry mixing, but one may also add some liquid, to improve the mixing. In this embodiment, the catalyst of the invention comprises a mixture of a zeolite based on rings having 12 oxygen atoms, wherein the zeolite ion-exchanged with palladium and is further loaded with one or more salts and/or oxides of scandium, yttrium, a lanthanide or a combination thereof. When salts are used, they will usually be converted into oxides, e.g. during a pretreatment.

The invention further comprises a method for the catalytic reduction of NO_x and a catalyst where the zeolite is loaded with one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system (c), in addition to (a) palladium and (b) scandium, yttrium, a lanthanide or a combination thereof. For example, the zeolite may be loaded with manganese, vanadium, niobium, gallium, indium, titanium, hafnium or stannum, but the zeolite may also be loaded with germanium, lead, zirconium, tantalum, chromium, molybdenum, tungstun, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, and platinum. Here the same applies as described above for scandium, yttrium, etc., viz. that the zeolite may be loaded by ion exchange, incipient wetness techniques or by physically mixing the zeolite with salts or oxides of said metals (see also below). Also combinations of these elements can be used, for example cobalt and platinum, or rhodium and molybdenum, manganese and cobalt, gallium and platinum, etc., or combinations of more than two metals from above-mentioned groups can be chosen. The zeolite may be loaded with 0-20 % by weight with one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system (c). Here, "% by weight" refers to the amount of zeolite exchanged with palladium (a) and loaded with oxides or salts (or both) of the metals from Sc, Y or a Ln (b) as well as the metal(s) from Group VIII of the periodic system (c).

The invention also encompasses in one embodiment a method for the catalytic reduction of NO_x and a catalyst where the zeolite is also loaded with 0.01-2% by weight of a second metal from Group VIII of the periodic system, in addition to palladium. Here, "% by weight" refers to the amount of zeolite exchanged with palladium (a) and loaded with the metal(s) as oxide(s) or salt(s) of Sc, Y or a Ln (b) and the second metal from Group VIII of the periodic system (c). Examples of such a metals are cobalt and platinum.

The present invention also encompasses a catalyst as described above.

The process conditions for the catalytic reduction of NO_x will depend on the applications. The person skilled in the art will therefore choose the catalyst volume, the gas speed, the temperature, the pressure and the quantity of methane (or natural gas), and the composition of the gas, in such a way that the best conversion results are achieved. Good results are achieved, for example, at an NO content of about 100 ppm or more. It is possible to work with an excess of methane. The NO_x/methane ratio is preferably between about 0.02 and 2.

The method can be used at relatively low temperatures. The conversion of NO_x takes place from about 300°C onwards. Almost complete conversion takes place at about 450°C. At higher temperatures the conversion may decrease somewhat, but good results are still achieved at 500°C. The temperature for working is preferably between 300°C and 600°C, more preferably between 350°C and 450°C.

The method according to the invention can *inter alia* be used for the catalytic reduction of NO_x which for example is emitted by gas engines, gas burners or emergency power supplies, or NO_x which is emitted during caprolactam production, etc.

Thus, gas burners are for example used in horticulture for CO_2 fertilization in greenhouses. A trace of NO_x can already impede the growth of the plants. In generating sets for emergency power supplies, use is usually made of diesel as fuel. In order to remove NO_x, according to the invention the reducing agent methane can be obtained from the natural gas network. In small-scale combined heat and power installations, gas turbines are also used in

addition to gas engines. In the case of these turbines, too, NO_x has to be removed from the outlet gases. The technique which makes use of natural gas as the reducing agent (instead of ammonia) is highly suitable for this purpose.

The method according to the invention can also be used in combination with a catalyst for the removal of N_2O, so that both NO_x and N_2O (laughing gas), which are emitted in the industrial production of nitric acid for example, are removed. A preferred embodiment of this comprises the method of the invention in combination with the catalyst for the removal of N_2O, wherein the latter is an iron-containing zeolite and/or a promoted iron-containing zeolite. In this process a gas containing nitrogen oxide (NO_x) and dinitrogen oxide (N_2O) is passed with methane through a first catalyst, as described above, and the gas obtained is then passed through an additional catalyst, where this additional catalyst comprises an iron-containing zeolite and/or a promoted iron-containing zeolite. The term "promoted" means that in addition to an active element, such as iron, the catalyst contains at least one additional element which promotes the reaction. Fe-ZSM-5 or Fe-MOR, for example, can be chosen as additional catalyst. The term "additional catalyst" refers to any extra catalyst, next to the catalyst of the invention. The person skilled in the art may also use a combination of additional catalysts.

NO_x and N_2O are also emitted in the production of caprolactam, a nylon precursor. The method described above of catalytic reduction of a gas containing nitrogen oxides and dinitrogen oxide with methane and the catalyst combination can also be used here.

The method according to the invention, as described above, can also be combined with other catalysts, e.g. catalysts for the removal of methane (such as PdO- or PtO-borne catalysts for example). Such a catalyst can be used to burn any methane left over after the catalytic reduction. The invention therefore also encompasses a method wherein an additional catalyst is used for the removal of methane, for example the combination of Ce-Pd-MOR and a PdO- or PtO-borne catalyst, or for example the combination of Ce-Pd-MOR, Fe-MOR and a PdO- or PtO-borne catalyst.

The present invention also encompasses a method for the preparation of a catalyst which is suitable for the catalytic reduction of NO_x from an NO_x containing gas using methane, as described above. In this method the zeolite is loaded with scandium, yttrium, a lanthanide or a combination thereof (and optionally other metals) after having been loaded with palladium by ion exchange (with the aid of a palladium salt in the liquid phase).

As mentioned above, the zeolite is loaded with scandium, yttrium, a lanthanide or a combination thereof by ion exchange, incipient wetness techniques or by physically mixing the zeolite with salts or oxides of these metals. The zeolite may be loaded with 0.01 to 50% by weight of these elements (present as oxide, salt or as ion). The person skilled in the art may choose the appropriate amounts of the metals. Here, "% by weight" refers to the amount of zeolite exchanged with palladium (a) and loaded with the metal(s) as oxide(s) or salt(s) of Sc, Y or a Ln (b).

When physical mixing is used to load the zeolite, the zeolite may usually be loaded with 0.01 to 50% by weight of scandium, yttrium, a lanthanide or a combination thereof. When ion exchange or incipient wetness techniques are used, the zeolite may usually comprise 0.01 to 20% by weight of scandium, yttrium, a lanthanide or a combination thereof. In a further embodiment, the zeolite is e.g. loaded with 0.01 to 20% by weight of these elements, more preferably with 1-10% by weight.

In a further embodiment of the method for the preparation of the catalyst according to the invention, a method may be used, where the zeolite, after having been loaded with palladium by ion exchange, the zeolite is optionally loaded with one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system, in addition to (a) palladium and (b) scandium, yttrium, a lanthanide or a combination thereof, before, at the same time or after the introduction of scandium, yttrium or a lanthanide or a combination thereof. The loading of the catalyst according to the invention with these metals can be done by ion exchange, incipient wetness techniques or by physically mixing the zeolite with salts or oxides of said metals. For example when using incipient wetness techniques, after the palladium exchange the zeolite can be loaded with 0.01 to 20%, e.g. 0.01-2% by weight of a

second metal from Group VIII of the periodic system, in addition to palladium, before, during or after the introduction of scandium, yttrium and/or lanthanide in the zeolite.

Known salts such as readily soluble nitrates, for example, are used for the palladium exchange. The H or NH_4 form of the zeolite, such as for example NH_4-MOR or H-FAU, etc., can for example be used as the zeolite. The exchange is performed long enough (or often enough) for about 0.02 to 2% by weight of palladium to be present in the zeolite. The zeolite is then filtered off, washed and dried. After that the zeolite is loaded with scandium, yttrium, a lanthanide or a combination thereof. This can be done by ion exchange or by pore volume impregnation (incipient wetness technique). After that the zeolite is dried and calcined. It can also be done by a physical mixing (see above).

Hence, the catalyst of the invention comprises a palladium-containing zeolite, wherein the palladium in the zeolite is wholly or partially coordinated as ion by the zeolite, wherein the zeolite is based on rings of 12 oxygen atoms, and wherein the zeolite is also loaded with scandium, yttrium or a lanthanide or a combination thereof, and wherein the zeolite is optionally also loaded with (c) one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system. This catalyst may be prepared and used in various embodiments, as shown in the table below:

	Pd ion	scandium, yttrium or a lanthanide or a combination thereof	optionally one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system
via ion exchange of the zeolite	X	X	X
via incipient wetness techniques	-	X	X
via physically mixing of the zeolite with a salt or oxide	-	X	X

One may also use a combination of methods, e.g. impregnating a Pd-exchanged zeolite with scandium, yttrium or a lanthanide or a combination thereof, and then further physically mixing with an oxide one of these metals.

Instead of physically mixing, or next to physically mixing, one may also use combinations of catalysts, e.g. a combination of catalysts where the catalysts are arranged in series. For example, the invention comprises also a method and a catalyst where the catalyst comprises a combination of (cat 1 (a)) a palladium-containing zeolite and (cat 2 (b)) an oxide of scandium, yttrium or a lanthanide or a combination thereof, in which the catalysts (cat 1 (a) and cat 2 (b)) are arranged in series. In another embodiment the invention comprises a method and a catalyst where the catalyst comprises a combination of a palladium-containing zeolite which has been loaded with scandium, yttrium or a lanthanide or a combination thereof by incipient wetness techniques (after the ion exchange with palladium) (cat 1(a,b) and an oxide of one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system (cat 2 (c)), in which the catalysts (1 (a,b) and 2 (c)) are arranged in series.

Here, the phrase "loaded with one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system, in addition to (a) palladium and (b) scandium, yttrium, a lanthanide or a combination thereof" describes that the zeolite is exchanged with palladium ions (a) and further loaded scandium, yttrium, a lanthanide or a combination thereof (b), either by ion-exchange, incipient wetness techniques or physical mixing with oxides or salts and also loaded with (c) one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system (either by ion-exchange, incipient wetness techniques or physical mixing with oxides or salts). The loading of the zeolite by palladium ions is always the first step. Then at the same time or after each other, the zeolite is loaded with one of the other metals (b,c). Since Pd should be exchanged first, "loaded with one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system in addition to palladium" means "loaded with one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system, with the exception of Pd. However, when a method is used, wherein an additional catalyst is used for the removal of

methane, Pd may be comprised as additional catalyst, which will be positioned in series after the catalyst of the invention (see also above). The catalyst of the invention comprises a palladium exchanged zeolite that is subsequently loaded with scandium, yttrium, a lanthanide or a combination thereof (b), either by ion-exchange, incipient wetness techniques or physical mixing (see above). Therefore, the phrase "loaded with one or more metals from groups IIIb, of the periodic system in addition to (b) scandium, yttrium, a lanthanide or a combination thereof" means that the catalyst of the invention comprises a zeolite that is "loaded with one or more metals chosen from the group consisiting of scandium, yttrium, and lanthanides (La and Lu inclusive) (b) and may optionally be loaded with one or more metals from group IIIb (belonging to (c)), wherein in the case of a loading with the same loading techniques the metals chosen from group (b) and group (c) will usually be different, and wherein in the case of a loading with the different loading techniques the metals chosen from group (b) and group (c) may be the same or may be different". Examples of loading with the same techniques are e.g. ion-exchange for metals chosen from (b) and ion-exchange for metals chosen from (c); or a physical mixing for metals chosen from (b) and a physical mixing for metals chosen from (c). For example, a zeolite is exchanged with palladium and then impregnated with cerium. The cerium-palladium zeolite may then physically be mixed with cerium oxide.

The invention is also directed to a catalyst that is obtainable according to method for the preparation of the catalyst of the invention.

Description of the figures

Figure 1: CH_4 and NO_x conversion over palladium-containing mordenite, wherein the mordenite is loaded with palladium by ion exchange (WIE) (Pd; catalyst 1) or impregnation (IMP) (Pd; catalyst 3).

Figure 2: FTIR absorption spectra of mordenite which has been impregnated with palladium (PdIMP) (Pd; catalyst 3), has been exchanged with palladium ions (PdWIE) (Pd; catalyst 1) and unloaded mordenite (HMOR).

Figure 3: NO_x conversions over palladium exchanged mordenite (Pd; catalyst 1), cerium loaded mordenite (Ce; catalyst 5), cobalt-palladium loaded mordenite (Co-Pd; catalyst 4) and cerium-palladium loaded mordenite (Ce-Pd; catalyst 2).

Figure 4: NO_x conversions over cerium-palladium loaded mordenite (catalyst 2) with methane as a function of time at different temperatures and gas speeds.

Figure 5: NO_x conversions over cerium-palladium loaded mordenite (catalyst 2) with methane as a function of time at 350°C and with a gas stream that is characteristic of the emissions of a nitric acid factory.

Figure 6: Conversions as a function of the temperature of a combined $deNO_x/deN_2O$ setup where the gas is first passed through catalyst 2 and then through catalyst 6. Methane is taken as the reducing agent; the gas stream is characteristic of the emissions of a nitric acid factory.

Examples

Test apparatus:

The catalytic conversion of NO, NO_2 (and possibly N_2O) with methane was studied in a semi-automatic test setup. Gases are supplied with so-called Mass Flow Controllers (MFC) and water is added by means of a saturator which has been set at the right temperature. Pipes are heated to 130°C in order to prevent condensation. A quartz reactor with an internal diameter of 0.6 to 1 cm is placed in an oven for the experiments. The catalyst sieve fraction (0.5-0.5 mm) is placed on a quartz gauze. Quantitative analysis of the gaseous phase is possible using a calibrated Bomen MB100 Fourier transform infra-red (FTIR) spectrometer equipped with a model 9100 gas analyser. The carrier gas (balance) in the examples is N_2.

Example 1: Preparation of loaded zeolites

Cat 1: Palladium-MOR (Pd-WIE)

Pd-MOR was prepared by ion exchange. NH_4-MOR powder (Zeolyst, CBV21a) was stirred for 24 h, at 80°C, in a 10% by weight $Pd(NO_3)_2$ in nitric acid (Aldrich, 10%) solution. After that the zeolite was filtered off, thoroughly washed with demineralized water and dried for 16 h at 80°C. (Pd(WIE)-MOR; here WIE stands for 'obtained with ion exchange').

Cat 2: Cerium-Palladium-MOR (Ce-IMP; Pd-WIE)

For the preparation of 4% by wt Ce(IMP)-0.4% by wt Pd(WIE)-MOR 5 grams of 0.4% by weight Pd(WIE)-MOR was then taken and 1 ml of cerium nitrate (Aldrich) was added to it with a density of 1.44 grams per ml. The pores were precisely filled with this quantity (incipient wetness). The impregnated zeolite was then dried for 16 h at 80°C and after that calcined in the reactor at 450°C.

Cat 3: Palladium MOR (Pd(IMP))

For the preparation of 0.4% by wt Pd(IMP)-MOR 5 grams of NH_4MOR was taken and 0.45 grams of 10% $Pd(NO_3)_3$ in 10% nitric acid was added to it. The impregnated zeolite was then dried for 16 h at 80°C and after that calcined in the reactor at 450°C. (PdIMP means impregnated with Pd).

Cat 4: Cobalt-Palladium MOR (Co(IMP)-Pd(WIE))

For the preparation of 2.3% by wt Co(IMP)-0.4% by wt Pd(WIE)-MOR 5 grams of Pd(WIE)-MOR was taken and 1 ml of cobalt nitrate (Aldrich) was added to it with a density of 1.38 grams per ml. The impregnated zeolite was then dried for 16 h at 80°C and after that calcined in the reactor at 450°C.

Cat 5: Cerium-MOR (Ce-IMP)

For the preparation of 4% by wt Ce(IMP)-MOR 5 grams of NH_4-MOR was taken and 1 ml of cerium nitrate (Aldrich) was added to it with a density of 1.44 grams per ml. The pores were precisely filled with this quantity (incipient wetness). The impregnated zeolite was then dried for 16 h at 80°C and after that calcined in the reactor at 450°C.

Cat 6: Fe-ZSM-5

This catalyst was prepared by the method of preparation described in NL-A-1017245.

Cat 7: Praseodimium-Palladium-MOR (Pr-IMP; Pd-WIE)

For the Pr-Pd combination catalysts, 1 ml of praseodymiumnitrate (9.375 gram dissolved in 10 ml demiwater) was added to 5 gram of Pd-MOR (Cat 1). In this case the pores of the

zeolite were precisely filled (so-called "incipient wetness impregnation"). Finally, the catalyst was dried for 16 h at 120 °C and calcined at 450 °C in situ.

Cat 8: Yttrium-Palladium-MOR (Pr-IMP; Pd-WIE)

For the Y-Pd combination catalysts, 1 ml of yttriumnitrate (11.5 gram dissolved in 10 ml demiwater) was added to 5 gram of Pd-MOR (Cat 1). In this case the pores of the zeolite were precisely filled (so-called "incipient wetness impregnation"). Finally, the catalyst was dried for 16 h at 120 °C and calcined at 450 °C in situ.

Cat 9: Physical mixture of an a Ln oxide and Cerium-Palladium-MOR (Ce-IMP; Pd-WIE)
As oxide of a lanthanide ceria (CeO_2) was chosen. Cat 8 and ceria were physical mixed (3:1 w/w).

Cat 10:BEA Ce-Pd

This catalyst was prepared in the same way as catalyst 2, but now using BEA as zeolite.

Cat 11:ZSM-5 Ce-Pd

This catalyst was prepared in the same way as catalyst 2, but now using ZSM-5 as zeolite.

Cat 12:FER Ce-Pd

This catalyst was prepared in the same way as catalyst 2, but now using FER as zeolite.

Example 2: Effect of preparation

Catalyst 1 and catalyst 3 were measured under the following test conditions, as given in Table 1. The results obtained are given in Table 2 and in Figure 1.

Table 1: test conditions for Example 2

Volume	0.9 ml
Flow	150 ml/min
GHSV	10000 h^{-1}
P	1 bara

Gas composition:	
NO	500 ppm
CH_4	2500 ppm
H_2O	5%
O_2	5%
N_2	balance

Table 2: conversion results from Example 2 (see also Figure 1)

	Cat 3			Cat 1	
T (°C)	CH_4 conversion (%)	NO_x conversion (%)		CH_4 conversion (%)	NO_x conversion (%)
202	0	0		0	0
222	1	0		0	0
242	1	0		0	0
261	2	0		0	0
281	1	0		1	0
302	4	3		1	4
322	4	1		1	9
342	5	6		5	17
362	8	10		5	31
382	12	16		8	39
402	24	23		10	48
422	43	33		10	61
443	71	38		15	67
463	99	36		29	76
483	100	30		58	81
503	100	19		91	83

From these data it is apparent that the Pd-impregnated catalyst (cat 3) burns methane, at the cost of the NO_x conversion. Such catalysts are therefore not suitable for the method of the invention.

Figure 2 gives FTIR absorptions of mordenite which has been loaded with palladium by ion exchange or impregnation, and of non-exchanged mordenite. Only in the case of the zeolite exchanged with palladium is an absorption band present at about 950 cm^{-1}, which is characteristic of Pd^{2+} at exchange sites.

Ion exchange with palladium results in a shift of the lattice vibrational band (± 1100-1000 cm^{-1}) towards lower wavenumber (between 980 and 920 cm^{-1}). As reported by e.g. L. Drozdova, R. Prins, J. Dedecek, Z. Sobalik, B. Wichterlova, J. Phys. Chem. B 106 (2002) 2240 and B. Pommier, P. Gélin, Phys. Chem. Chem. Phys. 1 (1999) 1665, this is indicative for palladium cations co-ordinated at the exchange site positions inside the zeolite micropores. This band is absent in the SCR inactive HMOR sample before introduction of palladium and in the SCR inactive catalyst prepared by impregnation with palladium (PdIMP).

The interaction of Pd^{2+} in the 12-membered ring channel of zeolite X and Y can also be shown by UV-VIS-NIR spectroscopy and ^{29}Si-MAS NMR (Sauvage et al., J. Chem. Soc. Faraday Trans. 1995, 91(18), 3291-3297 and Sauvage et al. Chem. Commun. 1996, 1325, respectively). However, also EXAFS may be used. For instance, Zhang and Sachtler describe in Zeolites Vol. 10, 1990 an EXAFS study that indicated the presence of Pd^{2+} in the12-membered ring of zeolite Y.

Example 3: Effect of promotors

In this example catalyst 2 (cerium-palladium-MOR: Ce-IMP; Pd-WIE), catalyst 3 (palladium-MOR: Pd-WIE), catalyst 4 (cobalt-palladium-MOR: Co-IMP; Pd-WIE) and catalyst 6 (cerium-MOR: Ce-IMP) are compared. The test conditions are as shown in Table 3, the results are given in Table 4 and in Figure 3.

Table 3: test conditions for Example 3

Volume	0.45 ml
Flow	150 ml/min
GHSV	20000 h^{-1}
P	1 bara
Gas composition:	
NO	500 ppm
CH_4	2500 ppm
H_2O	5%
O_2	5%
N_2	balance

Table 4: conversion results from Example 3 (see also Figure 3)

	NO_x conversion (%)			
T (°C)	Cat. 3 Pd	Cat. 6 Ce	Cat. 4 Co-Pd	Cat. 2 Ce-Pd
200	0	0	0	0
220	0	0	0	0
240	0	0	0	0
260	0	0	0	0
280	0	0	1	1
300	1	0	4	1
320	2	0	6	6
340	4	0	19	15
360	7	0	29	28
380	10	0	44	42
400	13	0	52	55
420	19	0	56	71
440	28	0	61	82
450	38	0	63	

	NO_x conversion (%)			
T (°C)	Cat. 3 Pd	Cat. 6 Ce	Cat. 4 Co-Pd	Cat. 2 Ce-Pd
470		0		
490		0		

From these data it is apparent that both cerium and cobalt increase the activity of Pd-MOR. Above about 400°C the conversion of the Ce-Pd-MOR catalyst is better. Ce-MOR does not show any activity at all, however, for the conversion of NO to N_2 with methane.

Example 4: Stability of Ce-Pd-MOR for exhaust gases from internal combustion engines

In this example the stability of catalyst 2 is measured at different gas speeds and at different temperatures. The test conditions are given in Table 5, and the results of measurement are given in Table 6 (also comparison with catalyst 4 Co(IMP)-Pd(WIE)-MOR) and are reproduced in Figure 4. The gas composition is characteristic of the composition of the exhaust gases from an internal combustion engine.

Table 5: test conditions for Example 4

Volume	0.45-1.8 ml
Flow	150 ml/min
GHSV	5000-20000 h^{-1}
P	1 bara
Gas composition:	
NO	500 ppm
CH_4	2500 ppm
H_2O	5%
O_2	5%
N_2	balance

From the results below (Table 6, Figure 4) it is apparent that in spite of the presence of 5% water (and 5% oxygen) the catalyst retains its activity at both temperatures. It is also

apparent from the comparison of cat 2 (Ce(IMP)-Pd(WIE)-MOR) and cat 4 (Co(IMP)-Pd(WIE)-MOR) in Table 6 that the stability of cat 2 is higher.

Table 6: conversion results from Example 4 (see also Figure 4 for Ce-Pd-MOR)

	Ce(IMP)-Pd(WIE)-MOR	Ce(IMP)-Pd(WIE)-MOR	Ce(IMP)-Pd(WIE)-MOR
Time (h)	T 370°C; 5000 h^{-1}	T 420°C; 20000 h^{-1}	T 420°C; 20000 h^{-1}
2	61	63	56
5	59	63	58
10	60	63	60
15	58	61	56
20	58	63	56
25	59	64	54
30	57	63	53
35	60	61	53
40	57	62	51
45	57	62	47
50	59	63	44
55	57		
60	58		
65	57		
70	58		
75	57		
80	59		

Example 5: Stability of Ce-Pd-MOR for nitric acid exhaust gas conditions

In this example catalyst 2 is used to remove NO_x from a gas composition such as is to be found in the outlet gases from a nitric acid factory. The conditions are given in Table 7 and the results in Table 8 and in Figure 5.

Table 7: test conditions for Example 5

Volume	15 ml
Flow	5 l/min
GHSV	20000 h^{-1}
P	4 bara
Gas composition:	
N_2O	1500 ppm
NO	500 ppm
CH_4	2500 ppm
H_2O	0.5%
O_2	2.5%
N_2	balance

Table 7: conversion results from Example 5 at 350°C (see also Figure 5)

Time (h)	NO_x (%)	Time (h)	NO_x (%)	Time (h)	NO_x (%)
0	67	34	62	68	63
2	66	36	62	70	62
4	65	38	62	72	62
6	66	40	62	74	61
8	65	42	62	76	62
10	64	44	62	78	61
12	63	46	62	80	62
14	63	48	62	82	62
16	62	50	62	84	62
18	63	52	61	86	62
20	62	54	62	88	61
22	62	56	62	90	61
24	62	58	63	92	62
26	63	60	62	94	61
28	63	62	63	96	61
30	62	64	62	98	61
32	62	66	62		

From these results (Table 8, Figure 5) it is apparent that the catalyst retains its activity for a long time at 350°C in the presence of 0.5% water (and 2.5% oxygen) and 1500 ppm N_2O.

Example 6: Combined NO_x-N_2O removal

In this example a combined deNO_x–deN_2O setup is used, as described in NL-A-1017245, and in which the first catalyst is now catalyst 2 and the second catalyst is catalyst 6. Methane is used as reduction gas. The reaction conditions are given in Table 8, and are as in outlet gases from a nitric acid factory. The test results are shown in Table 9 and are also given in Figure 6. From the results it is apparent that good NO_x and N_2O conversions can be achieved at relatively low temperatures. Even better conversions are achieved at pressures higher than 1 bara (Figure 6a: N_2O conversion at 1 and 6 bara; Figure 6b: NO_x conversion at 1 and 4 bara).

Table 8: test conditions for Example 6

	Cat 2	Cat 6
Volume	15 ml	15 ml
Flow	5 l/min	
GHSV	20000 h^{-1}	
P	1 and 4 bara	
Gas composition:		
N_2O	1500 ppm	
NO	500 ppm	
CH_4	2500 ppm	
H_2O	0.5%	
O_2	2.5%	
N_2	balance	

Table 9: NO_x and N_2O conversion results from Example 6 (see also Figure 6a and 6b)

	1 bara		4 bara	
T (°C)	N_2O (%)	NO_x (%)	N_2O (%)	NO_x (%)
263	0	5	0	19
290	1	7	1	20
318	7	12	10	28
346	26	24	47	57
375	61	41	98	94
405	95	63	100	100
436	100	82	98	100
466	100	88	100	99

Example 7: Conversion of NO_x and CH4 and stability of Y-Pd-MOR

Catalyst 8 was measured for evaluation of the conversion and stability, under the test conditions as given in Tables 10 and 12, respectively. The results obtained are given in Tables 11 and 13, respectively.

Table 10: test conditions for Example 7 (conversion)

Example CH_4-SCR: performance yttrium-Pd-MOR	
Volume	0.45 ml
Flow	100 ml/min
GHSV	13500 h-1
P	1 bara
Gascomposition	
NO	500 ppm
CH_4	2500 ppm
H_2O	5 %
O_2	5%
N_2	bal.

Table 11: conversion results for Pr-Pd-MOR (Cat 8)

	Yttrium-Pd-MOR	
T (°C)	CH_4 %	NO_x %
260	0	0
281	0	0
302	0	0
322	0	0
342	1	3
362	2	5
382	3	13
392	3	18
412	4	27
433	9	50
453	22	85
473	55	98
490	89	100

Table 12: test conditions for Example 7 (stability)

Example CH_4-SCR: performance yttrium-Pd-MOR	
Volume	0.9 ml
Flow	100 ml/min
GHSV	7000 h^{-1}
T	395 °C
P	1 bara
Gascomposition	
NO	500 ppm
CH_4	2500 ppm
H_2O	10.5%
O_2	5%
N_2	bal.

Table 13: Performance for Y-Pd-MOR (Cat 8): conversion at 400 °C as a function of time

T 400 °C; 7.000 h^{-1}	Conversion (%)	
Time (h)	CH_4	NO_x
2	10	58
100	9	53
150	10	54
200	10	55
250	9	54
300	11	56
350	9	54
400	10	55
450	11	52

Yttrium (yttria) improves the SCR activity of palladium-MOR resulting to higher NO_x conversion level as compared to palladium. Yttrium (yttria) stabilizes Pd-MOR, even in the presence of over 10 % water in the feed.

Example 8: Stability of Pr-Pd-MOR

Catalyst 7 was measured for evaluation of the stability, under the test conditions as given in Table 14. The results obtained are given in Table 15.

Table 14: test conditions for Example 8 (Stability)

Example CH_4-SCR: Stability Praseodymium-Pd-MOR	
Volume	0.7 ml
Flow	100 ml/min
GHSV	9.000 h-1
T	420 deg C
P	1 bara
Gascomposition	

NO	500 ppm
Ch_4	2500 ppm
H_2O	5%
O_2	5%
N_2	bal.

Table 15: Performance for Pr-Pd-MOR (Cat 7): conversion at 420 °C as a function of time

T 420 °C; 9.000 h^{-1}	Conversion (%)	
Time (h)	CH_4	NO_x
2	11	59
10	14	60
23	14	63
80	14	65
85	15	64

Praseodymium improves the SCR activity of palladium-MOR resulting in a higher NO_x conversion level as compared to palladium alone. Praseodymium stabilizes Pd-MOR and shows no signs of deactivation for the period of the test (85 hour).

Example 9: Conversion of NO_x and CH_4 on a number of palladium exchanged mordenites

A number of palladium exchanged mordenites were measured for evaluation of the conversion, under the test conditions as given in Table 16. The results obtained are given in Table 17. The lanthanum (La), dysprosium (Dy) and gadolinium (Gd) Pd-mordenites were prepared in the same way as described for Cat 7 and 8.

Table 16: test conditions for Example 9 (conversion)

Example CH_4-SCR: performance Lanthanides-Pd-MOR	
Volume	0.45 ml
Flow	100 ml/min
GHSV	13500 h-1
P	1 bara

Gascomposition	
NO	500 ppm
CH_4	2500 ppm
H_2O	5 %
O_2	5%
N_2	bal.

Table 17: conversion of NO_x and CH_4 on Pd-exchanged mordenites

	Pd-MOR		Pr-Pd-MOR		Tb-Pd-MOR		La-Pd-MOR		Dy-Pd-MOR		Gd-Pd-MOR	
T (°C)	CH_4 %	NO_x %	CH_4 %	NO_x %	CH_4 %	NO_x %	CH_4 %	NO_x %	CH_4 %	NO_x %	CH_4 %	NO_x %
259	0	0	0	0	nd	nd	0	0	0	0	0	0
269	0	0	0	0	nd	nd	0	0	0	0	0	0
279	0	0	0	0	nd	nd	0	0	0	0	0	0
288	0	0	0	0	nd	nd	0	0	0	0	0	0
298	0	0	0	0	0	0	0	0	0	0	0	0
308	0	0	0	0	0	0	0	0	0	0	0	0
318	0	0	0	0	0	0	1	0	0	0	0	0
328	0	0	0	0	0	0	1	4	1	1	2	4
338	2	7	2	9	0	0	2	9	2	5	3	3
348	1	8	2	11	0	0	3	9	2	2	3	5
357	3	8	3	10	0	4	3	11	2	6	5	6
367	8	11	4	11	1	5	3	13	2	9	4	8
377	5	13	4	12	1	8	3	15	3	11	4	11
387	5	15	3	14	4	8	3	18	2	10	3	13
397	4	17	6	15	5	14	4	21	4	16	4	14
406	5	21	7	22	5	15	5	25	4	21	6	17
416	7	23	10	24	4	17	7	29	7	26	4	17
426	9	25	8	27	5	20	8	37	7	35	8	22
436	17	30	11	38	7	24	12	48	10	50	10	29
445	21	41	14	66	11	37	18	57	16	67	16	48
455	29	54	27	82	15	53	27	71	24	87	22	75
464	45	70	42	100	24	81	42	80	39	94	36	90
474	72	79	59	100	35	99	68	86	59	97	54	99
483	94	79	77	100	53	100	94	89	78	97	71	97
493			90	100	72	100	100	86	93	99	93	100

Lanthanides improve the SCR activity of palladium-MOR resulting in higher NO_x conversion levels as compared to palladium mordenite (ion exchanged) only.

Example 10: Conversion of NO_x and CH_4 on a physical mixture of a zeolite and an oxide (Cat 9)

Cat 9 was measured for evaluation of the conversion, under the same test conditions as given in Table 16. The results obtained are given in Table 18.

Table 18: conversion results for Cat 9

	CeO_2 + Yttrium-Pd-MOR	
T (°C)	CH_4 %	NO_x %
260	0	0
281	0	0
302	0	0
318	5	19
338	8	45
362	15	72
377	20	88
387	22	92
407	26	94
427	33	99
456	50	99
475	67	99
495	91	99

Physical mixing of ceria and Y-Pd-CBV21a (1:3 w/w) gives a very high SCR activity.

Example 11: Conversion of NO_x and CH_4 on BEA (Cat 10) compared to ZSM-5 (Cat 11)

Ce-Pd-BEA (Ce IMP; Pd WIE) Cat 10 was measured for evaluation of the conversion in comparison to Ce-Pd-ZSM-5 (Ce IMP; Pd WIE) (Cat 11), under the same test conditions as given in Table 3. The results obtained are given in Table 19.

Table 19: conversion results for Ce-Pd-BEA (Ce IMP; Pd WIE) Cat 10 and Ce-Pd-ZSM-5 (Ce IMP; Pd WIE) (Cat 11)

	cerium-Pd-ZSM-5 (10-ring)		cerium-Pd-BEA (12-ring)	
T (°C)	CH_4 %	NO_x %	CH_4 %	NO_x %
276	0	0	0	0
295	0	0	0	0
315	0	0	0	0
334	1	6	1	8
353	3	9	4	14
372	4	15	5	17
391	5	22	7	24
410	10	26	12	30
430	15	32	18	35
450	22	33	24	49

Compared to Ce(IMP)-Pd(WIE)-ZSM-5 (10-ring zeolite), the Ce(IMP)-Pd(WIE)-BEA catalyst (12-ring zeolite) is more active for NO_x SCR with methane.

Example 12: Conversion of NO_x and CH_4 on Ce-Pd-ZSM-5 and stability of Ce-Pd-ZSM-5 (not according to the invention)

Ce-Pd-ZSM-5 (Ce IMP; Pd WIE) Cat 11 was measured for evaluation of the conversion and performance (stability), under the test conditions as given in Table 3 (with 19500 instead of 20000 h^{-1}) and table 21, respectively. The results obtained are given in Tables 20 and 22, respectively.

Table 20: conversion results for Ce-Pd-ZSM-5 (Ce IMP; Pd WIE) Cat 11

	cerium-Pd-ZSM-5	
T (°C)	CH_4 %	NO_x %
199	0	0
219	0	0
238	0	0
257	0	0
276	0	0
295	0	0
315	0	0
334	1	6
353	3	9
372	4	15
391	5	22
410	10	26
430	16	32
450	22	33

Table 21: test conditions for Ce-Pd-ZSM-5 (Ce IMP; Pd WIE) Cat 11 (Stability)

Example CH_4-SCR: stability of Ce-Pd-ZSM-5 as a function of the temperature	
Volume	0.45 ml
Flow	150 ml/min
GHSV	19.500 h-1
T	450 °C
P	1 bara

Table 22: test results for Ce-Pd-ZSM-5 (Ce IMP; Pd WIE) Cat 11 (Stability)

Time (h)	CH_4(%)	NO_x (%)
2	18	23
5	14	18
10	13	16
15	12	12
20	11	12
25	11	12
30	10	11
35	9	11
40	8	9
45	7	8
50	7	7

It appears that the Ce(IMP)-Pd(WIE)-ZSM5 catalyst is not very active compared to Ce-Pd-MOR and even deactivates with time.

Example 13: Conversion of Ce-Pd-FER (not according to the invention)

Ce-Pd-FER (Ce IMP; Pd WIE) Cat 12 was measured for evaluation of the conversion and performance (stability), under the test conditions as given in Table 10. The results obtained are given in Table 23.

Table 23: conversion of NO_x and CH_4 on Ce-Pd-FER (Ce IMP; Pd WIE) Cat 12

	cerium-Pd-FER (10/8 ring)		
T (°C)	CH_4 %	NO_2 %	NO_x %
200	0	0	0
219	0	0	0
238	0	0	0
258	0	3	0
277	0	4	0
297	0	7	0

	cerium-Pd-FER (10/8 ring)		
T (°C)	CH_4 %	NO_2 %	NO_x %
316	1	10	0
335	2	12	0
355	2	14	0
374	2	22	0
393	2	19	0
412	3	27	0
431	6	23	0

The Ce(IMP)-Pd(WIE)-FER catalyst is only active for the oxidation of NO to NO_2. However, NO_x (including NO_2 that has been obtained after the conversion by this catalyst), is not reduced at all.

Claims

1. A method for the catalytic reduction of NO_x in an NO_x containing gas using methane in the presence of a catalyst which comprises a palladium-containing zeolite, characterized by using a zeolite based on rings having 12 oxygen atoms, wherein the zeolite also contains scandium, yttrium, a lanthanide or a combination thereof.

2. Method according to Claim 1, wherein the zeolite is loaded with scandium, yttrium, a lanthanide or a combination thereof and optionally other metals after having been loaded with palladium by ion exchange.

3. Method according to one of Claims 1 and 2, wherein the zeolite comprises a zeolite of the class of FAU, MOR, BEA, EMT, CON, BOG or ITQ-7.

4. Method according to Claim 3, wherein the zeolite is MOR.

5. Method according to one of Claims 1-4, wherein the zeolite is loaded with 0.02 to 2% by weight of palladium.

6. Method according to one of Claims 1-5, wherein the zeolite is loaded with scandium, yttrium, a lanthanide or a combination thereof by ion exchange or incipient wetness techniques.

7. Method according to Claim 6, wherein the zeolite comprises 0.01 to 20% by weight of scandium, yttrium, a lanthanide or a combination thereof.

8. Method according to one of Claims 1-5, wherein the zeolite is loaded with scandium, yttrium, a lanthanide or a combination thereof by physically mixing the zeolite with salts or oxides of said metals.

9. Method according to Claim 8, wherein the zeolite is loaded with 0.01 to 50% by weight of scandium, yttrium, a lanthanide or a combination thereof.

10 Method according to one of claims 1-9, wherein the zeolite is loaded with one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system, in addition to palladium and scandium, yttrium, a lanthanide or a combination thereof.

11. Method according to one of Claims 1-10, wherein the gas also comprises oxygen and/or water.

12. Method according to one of Claims 1-11, wherein the gas also comprises carbon monoxide.

13. Method according to one of Claims 1-12, wherein the reaction temperature is between 300°C and 600°C, and the NO_x/methane ratio is between 0.02 and 2.

14. Method according to one of Claims 1-13, wherein an additional catalyst is used for the removal of N_2O.

15. Method according to Claim 14, wherein the catalyst for the removal of N_2O is an iron-containing zeolite and/or a promoted iron-containing zeolite.

16. Method according to one of Claims 1-15, wherein an additional catalyst is used for the removal of methane.

17. Catalyst which comprises a palladium-containing zeolite, wherein the palladium in the zeolite is wholly or partially coordinated as ion by the zeolite, wherein the zeolite is based on rings of 12 oxygen atoms, and wherein the zeolite is also loaded with scandium, yttrium or a lanthanide or a combination thereof.

18. Catalyst according to Claim 17, characterized by an infra-red sensitive zeolite lattice vibration visible at about 950 cm^{-1}.

19. Catalyst according to Claims 17 or 18, wherein the zeolite is loaded with one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system, in addition to palladium and scandium, yttrium, a lanthanide or a combination thereof.

20. Method for the preparation of a catalyst which comprises a palladium-containing zeolite based on rings having 12 oxygen atoms and wherein the zeolite also comprises scandium, yttrium or a lanthanide or a combination thereof, wherein the zeolite is loaded with scandium, yttrium, a lanthanide or a combination thereof and optionally other metals after having been loaded with palladium by ion exchange.

21. Method according to Claim 20, wherein the zeolite, after having been loaded with palladium by ion exchange, the zeolite is loaded with one or more metals from groups IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, and VIII of the periodic system, in addition to palladium and scandium, yttrium, a lanthanide or a combination thereof, before, at the same time or after the introduction of scandium, yttrium or a lanthanide or a combination thereof.

Fig 1

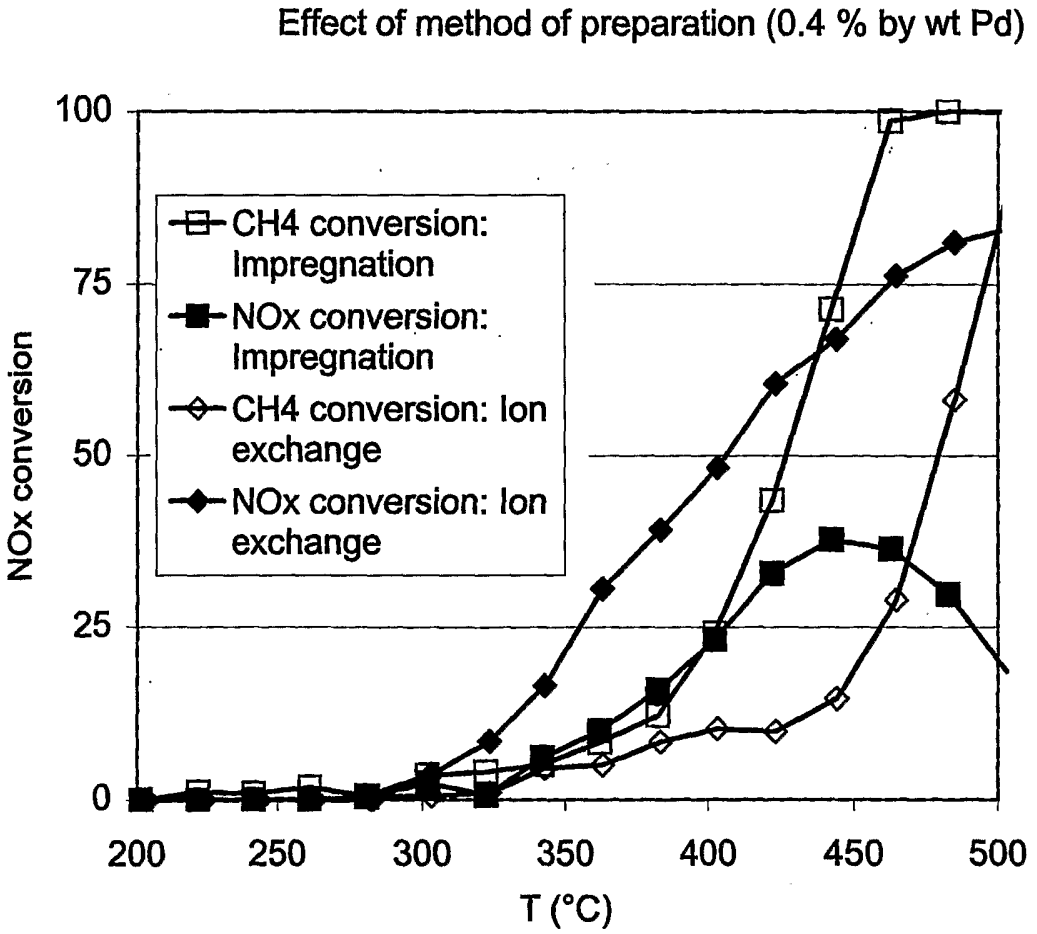

Effect of method of preparation (0.4 % by wt Pd)
NOx conversion
100
75
50
25
0
200
250
300
350
400
450
500
T (°C)
CH4 conversion: Impregnation
NOx conversion: Impregnation
CH4 conversion: Ion exchange
NOx conversion: Ion exchange

Fig 2

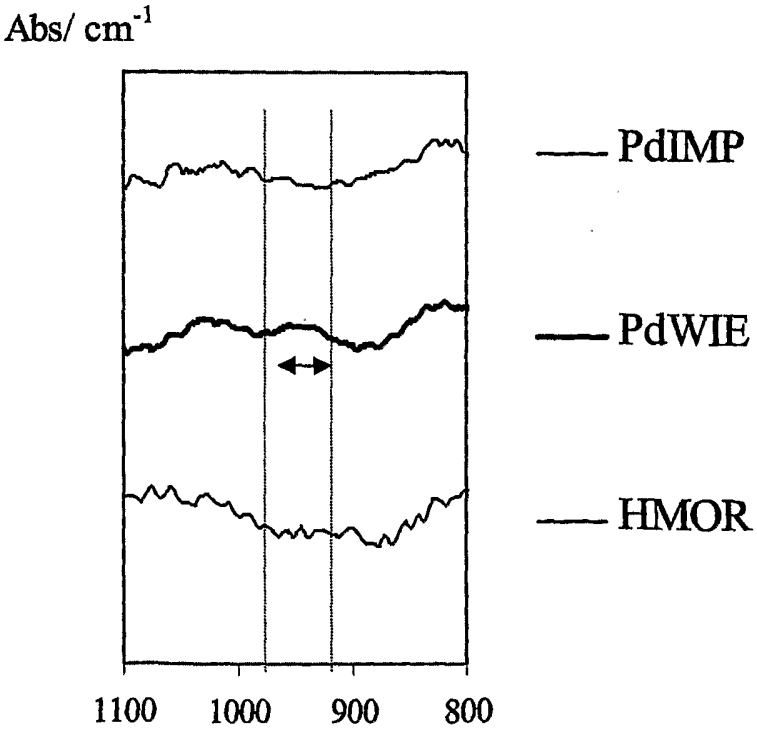

Abs/ cm-1
PdIMP
PdWIE
HMOR
1100
1000
900
800

Fig 3

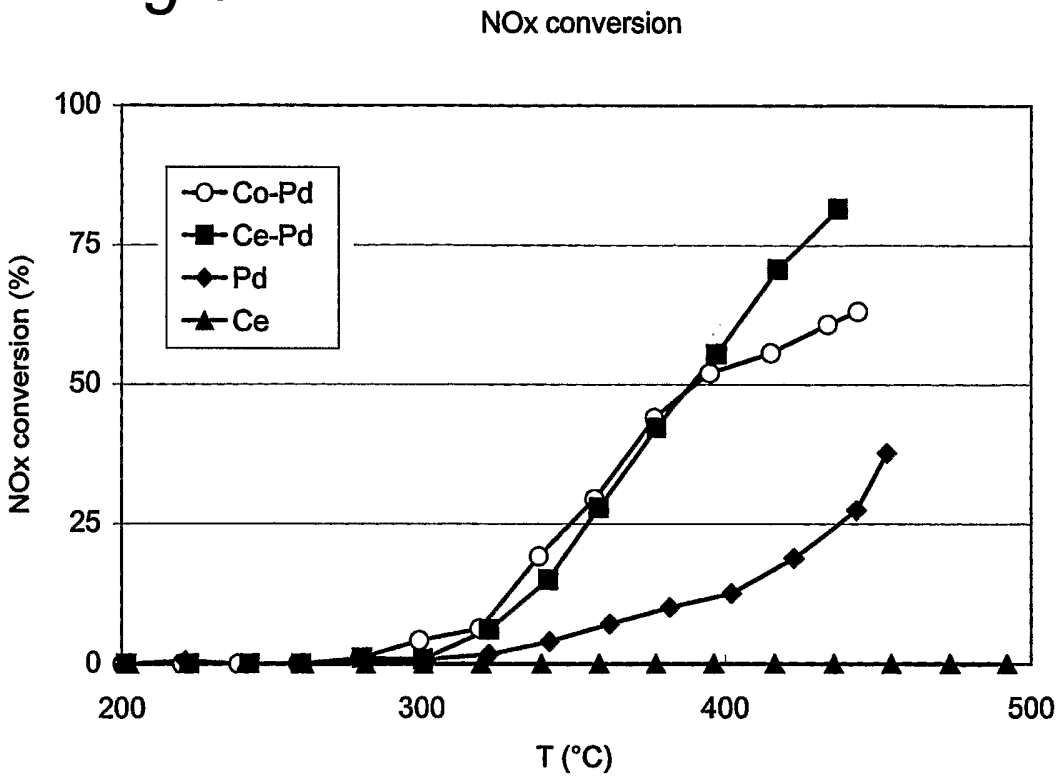

NOx conversion
100
75
50
25
0
NOx conversion (%)
Co-Pd
Ce-Pd
Pd
Ce
200
300
400
500
T (°C)

Fig 4

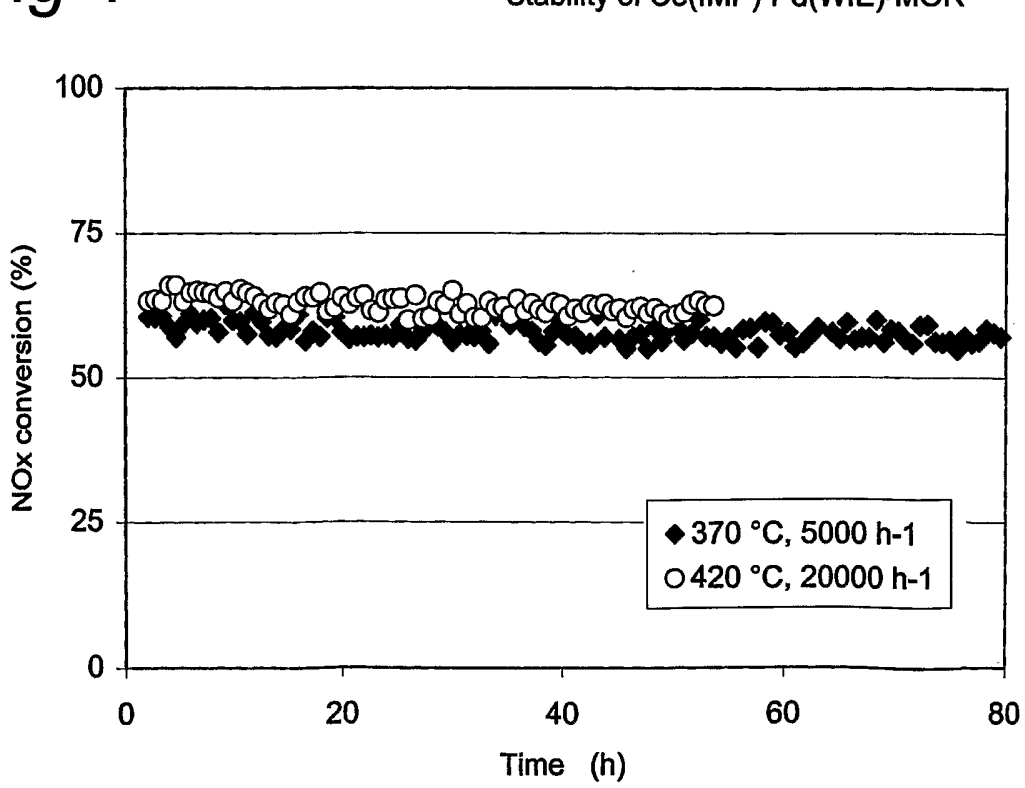

Stability of Ce(IMP)-Pd(WIE)-MOR
100
75
50
25
0
NOx conversion (%)
370 °C, 5000 h-1
420 °C, 20000 h-1
0
20
40
60
80
Time (h)

Fig 5

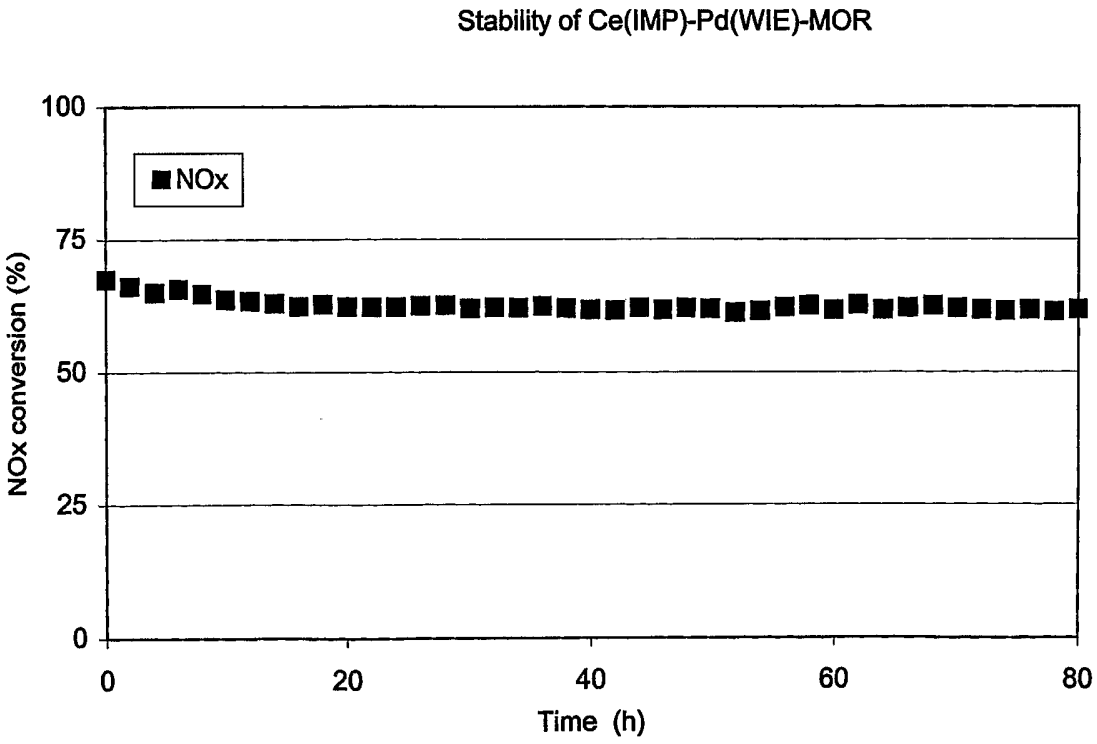

Stability of Ce(IMP)-Pd(WIE)-MOR
NOx
NOx conversion (%)
100
75
50
25
0
0
20
40
60
80
Time (h)

Fig 6a

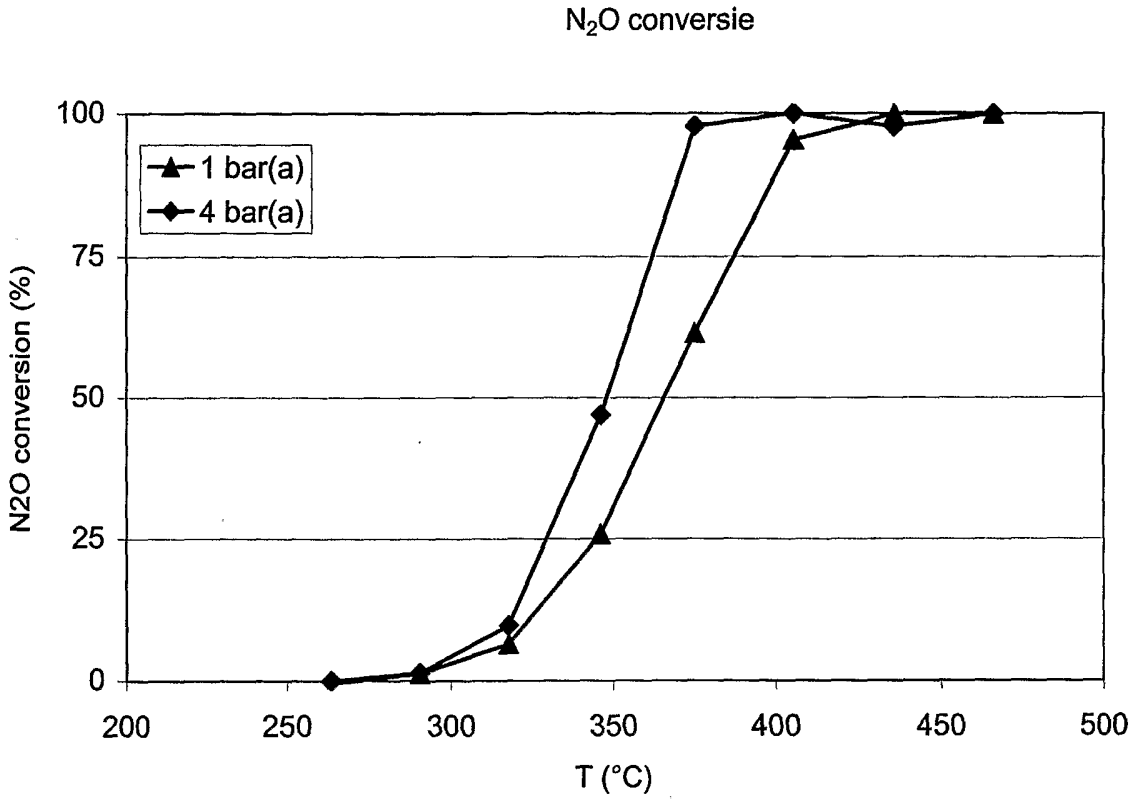
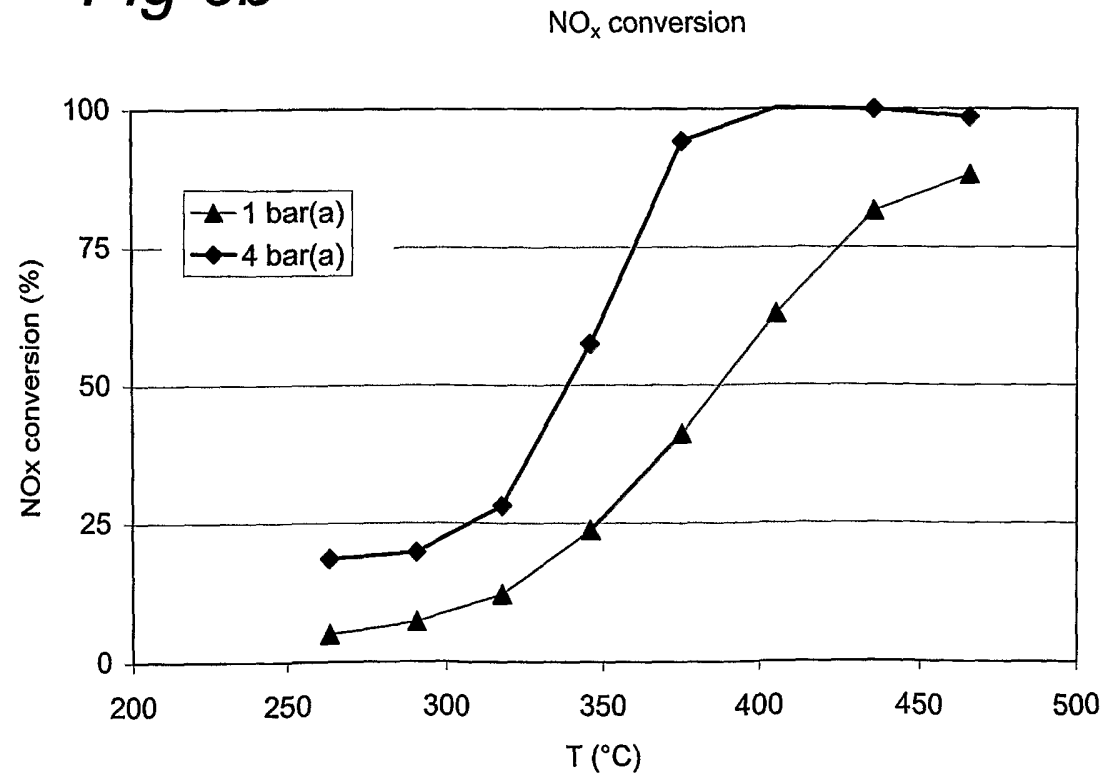

N_2O conversie
100
75
50
25
0
N2O conversion (%)
1 bar(a)
4 bar(a)
200
250
300
350
400
450
500
T (°C)

Fig 6b


NO_x conversion
100
75
50
25
0
NOx conversion (%)
1 bar(a)
4 bar(a)
200
250
300
350
400
450
500
T (°C)

INTERNATIONAL SEARCH REPORT

Internat plication No
PCT/NL 03/00532

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/86 B01J29/06

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)
PAJ, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 11, 28 November 1997 (1997-11-28) & JP 09 192486 A (MAZDA MOTOR CORP), 29 July 1997 (1997-07-29) abstract ---	17-21
X	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 10, 31 October 1996 (1996-10-31) & JP 08 164338 A (MAZDA MOTOR CORP), 25 June 1996 (1996-06-25) abstract --- -/--	17-21

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
28 August 2003	04/09/2003

Name and mailing address of the ISA	Authorized officer
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PCT/NL 03/00532

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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