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(54) **PROCESS AND APPARATUS FOR PURIFYING EXHAUST GASES FROM AN INTERNAL COMBUSTION ENGINE**

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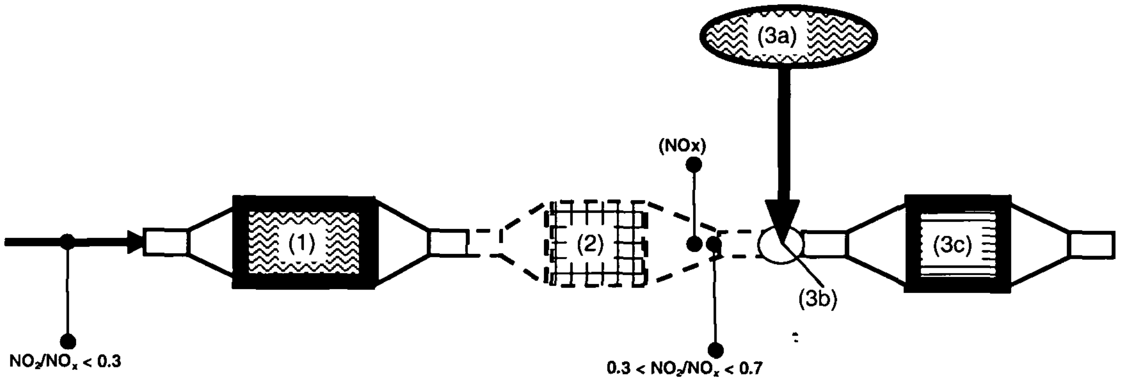
(57) **ABSTRACT**

The present invention relates to a process for purifying NO_x-containing exhaust gases formed in an internal combustion engine. In particular, the invention is directed at the purification of exhaust gases from an engine which produces a lean-burn exhaust gas, e.g. a diesel engine or a spark-ignition engine operated under lean conditions. Furthermore, the present invention relates to an appropriately equipped exhaust gas purification apparatus. The apparatus proposes a sequence of different catalysts for purifying primary axhaust gas of lean-burn engines, in which an oxidatively active particle filter (**1**) is followed by an oxidation catalyst (**2**) and this is in turn followed by an SCR catalyst, (**3***c*) with the latter being arranged downstream of an addition of reducing agent (**3***a*) located downstream of the oxidation catalyst (**2**).



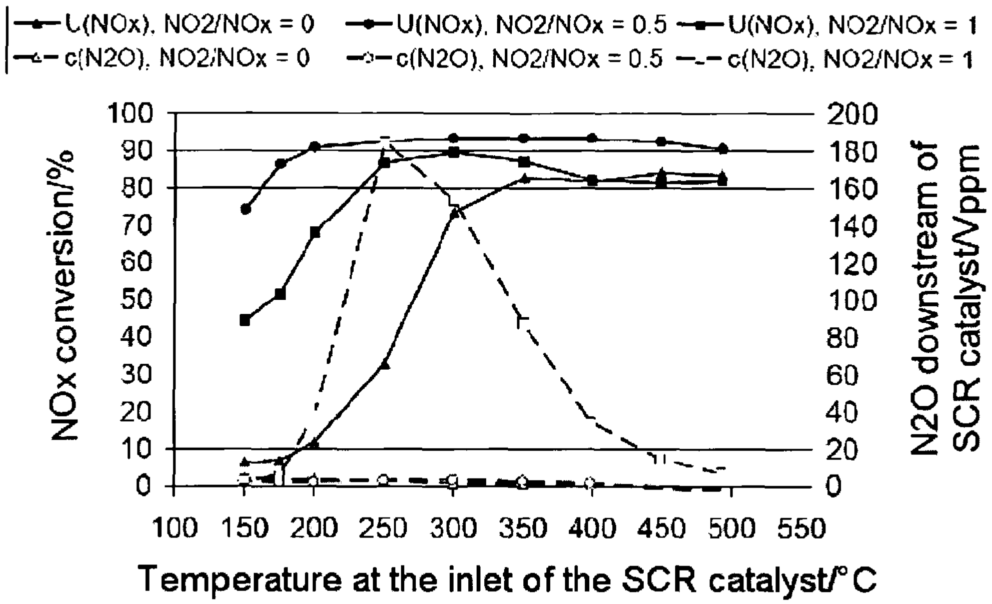


Figure 1

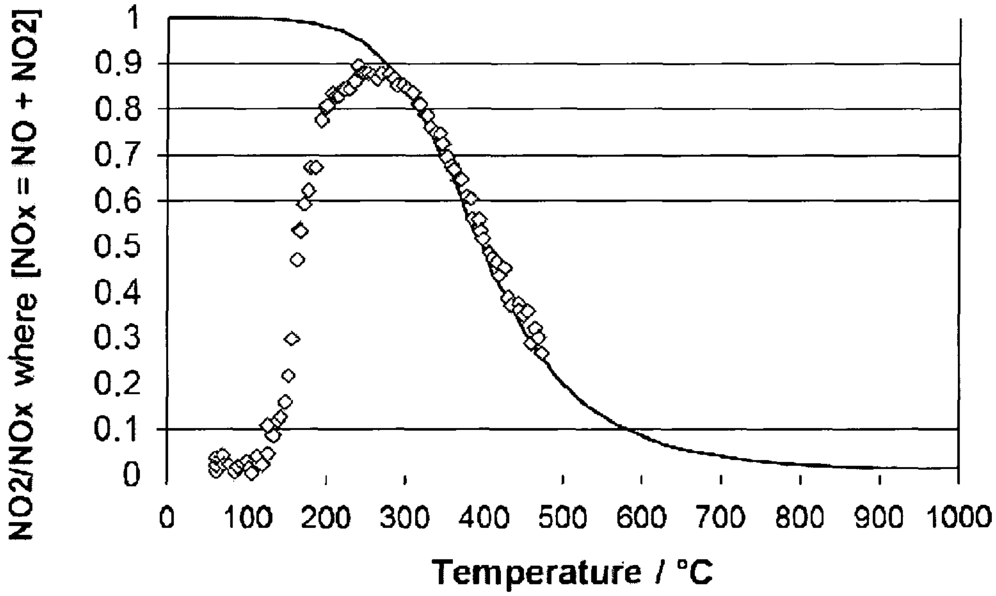


Figure 2

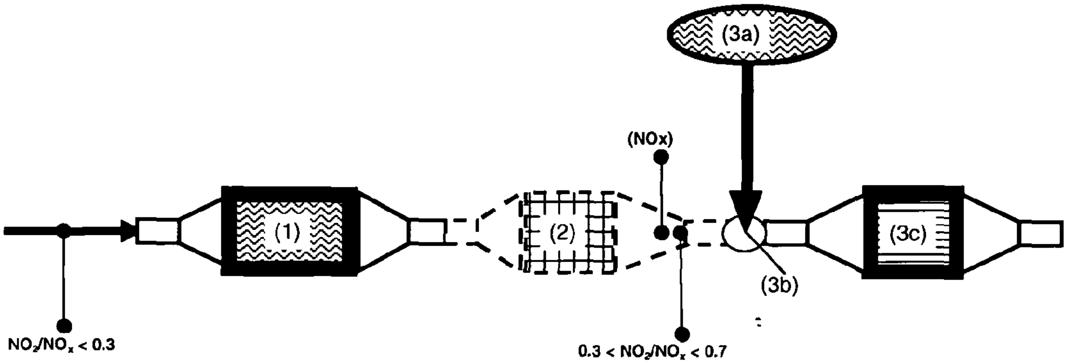


Figure 3

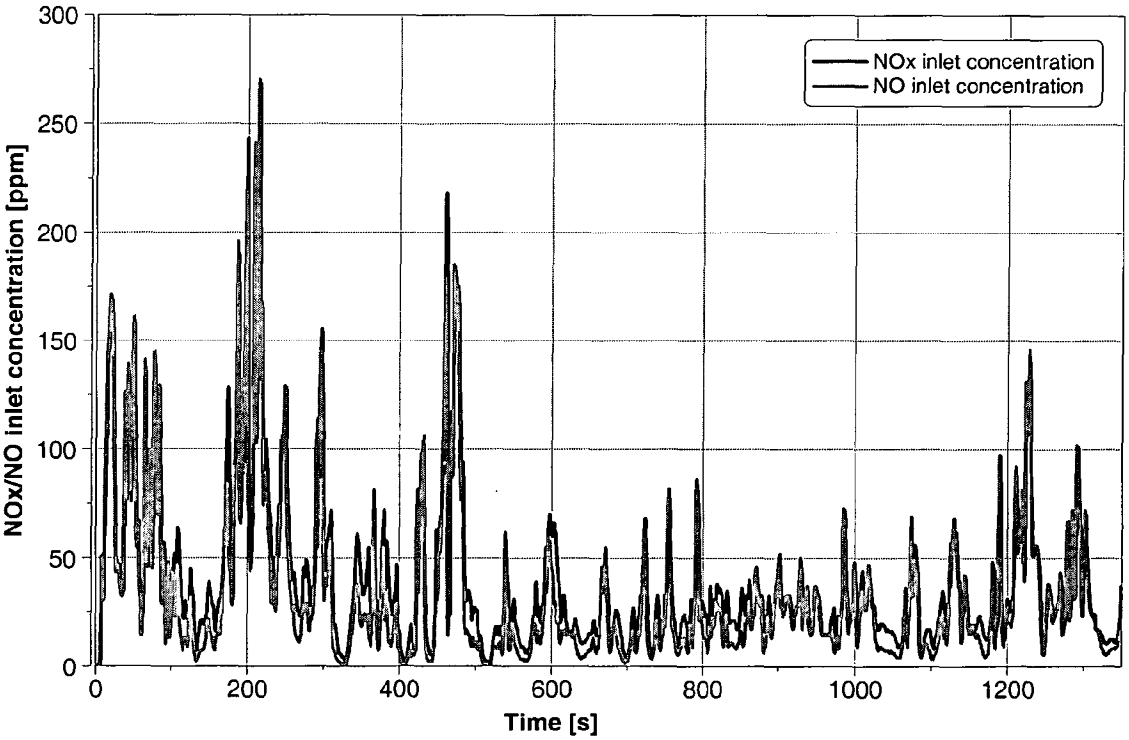


Figure 4

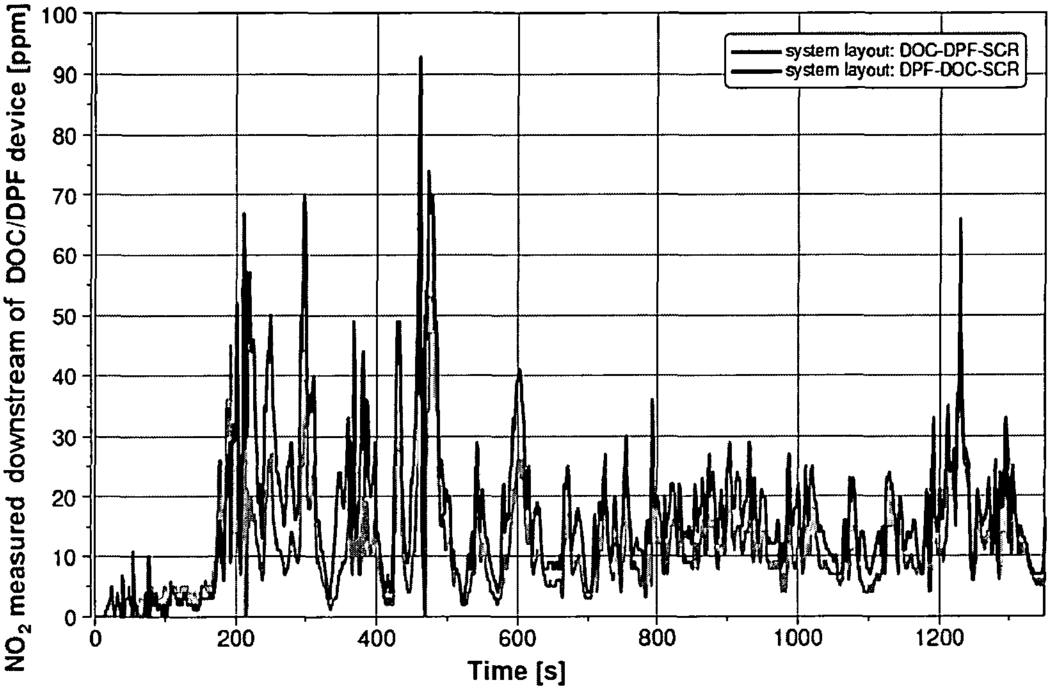

system layout: DOC-DPF-SCR
system layout: DPF-DOC-SCR
NO2 measured downstream of DOC/DPF device [ppm]
100
90
80
70
60
50
40
30
20
10
0
0
200
400
600
800
1000
1200
Time [s]

Figure 5

PROCESS AND APPARATUS FOR PURIFYING EXHAUST GASES FROM AN INTERNAL COMBUSTION ENGINE

[0001] The present invention relates to a process for purifying NO_x-containing exhaust gases from a combustion process. In particular, the invention is directed at the purification of exhaust gases from an engine which produces a lean-burn exhaust gas, e.g. a diesel engine or a spark-ignition engine operated under lean conditions. Furthermore, the present invention relates to an exhaust gas purification apparatus equipped for carrying out the process of the invention.

[0002] The emissions present in the exhaust gas of a motor vehicle can be divided into two groups. Thus, the term primary emission refers to pollutant gases which are formed directly by the combustion process of the fuel in the engine and are present in the raw exhaust gas at the outlet from the cylinder. The term secondary emission refers to pollutant gases which can be formed as by-products in the exhaust gas purification system. The raw exhaust gas from lean-burn engines not only contains the usual primary emissions carbon monoxide (CO), hydrocarbons (HCS) and nitrogen oxides (NO_x) but also has a relatively high oxygen content of up to 15% by volume. In addition, there can also be particle emissions which comprise predominantly soot residues and possibly organic agglomerates and originate from incomplete combustion of the fuel in the cylinder.

[0003] Adherence to legal exhaust gas limits which will in future apply to vehicles in Europe, North America and Japan requires not only the removal of particles but also effective removal of nitrogen oxides from the exhaust gas ("deNOx"). The pollutant gases carbon monoxide and hydrocarbons in the lean-burn exhaust gas can easily be rendered nonpolluting by oxidation of a suitable oxidation catalyst. Apparatuses suitable for the removal of the particle emissions are particle filters with and without an additional catalytically active coating. The reduction of the nitrogen oxides to nitrogen is more difficult because of the high oxygen content of the exhaust gas from internal combustion engines operated under lean conditions. Known processes are either based on the use of nitrogen oxide storage catalysts (NO_x storage catalyst, NSC) or are processes for selective catalytic reduction (SCR), usually by means of ammonia as reducing agent, over a suitable catalyst, known as SCR catalyst for short. Combinations of these processes in which, for example, ammonia is generated as secondary emission over an upstream nitrogen oxide storage catalyst under rich operating conditions, the ammonia is firstly stored in a downstream SCR catalyst and utilized in a subsequent lean-burn operating phase for the reduction of the nitrogen oxides passing over the nitrogen oxide storage catalyst. DE 102007060623 describes a series of variants of exhaust gas purification systems having deNOx facilities which are known in the prior art.

[0004] The use of such "passive processes" for the removal of nitrogen oxides from lean-burn engine exhaust gases is limited by, in particular, the fact that the provision of rich operating phases is not readily possible, especially in the case of diesel engines. Thus, the regeneration of nitrogen oxide storage catalysts (desorption with simultaneous reduction of the desorbed nitrogen oxides to nitrogen) and the generation of an internal reducing agent (NH_3, possibly also HCs or CO) as required by an SCR catalyst for the conversion of NO_x can be achieved only with the aid of auxiliary measures such as injection of fuel into the exhaust gas train or into the cylinder during the exhaust stroke of the piston. Such auxiliary measures lead to an undesirable increased consumption of fuel and also make it more difficult to adhere to the legal limits for CO and HCs.

[0005] Accordingly, the "active" SCR process is at present the preferred process for the removal of nitrogen oxides from lean-burn engine exhaust gases. Here, the amount of nitrogen oxides present in the exhaust gas is decreased with the aid of a reducing agent introduced into the exhaust gas train from an external source. Ammonia or a compound which can be decomposed into ammonia, e.g. urea or ammonium carbamate, is preferably used as reducing agent. The ammonia, which may have been generated in situ from the precursor compound, reacts over the SCR catalyst with the nitrogen oxides in the exhaust gas in a comproportionation reaction to form nitrogen.

[0006] It is known that the efficiency of the SCR catalyst increases with increased amount of reducing agent. However, the risk of NH_3 breakthrough over the SCR catalyst also increases with increased NH_3 content.

[0007] Furthermore, optimal nitrogen oxide conversions are achieved only when nitrogen monoxide and nitrogen dioxide are present in equimolar amounts ($NO/NO_2=1$) or the ratio of $NO_2/NO_x=0.5$ (G. Tuenter et al., Ind. Eng. Chem. Prod. Res. Dev. 1986, 25, 633-636; FIG. 1). FIG. **1** shows, by way of example, model gas results of a conventional SCR catalyst based on an iron-exchanged zeolite which illustrate the dependence of the nitrogen oxide conversion and the selectivity of the reaction on the NO_2/NO_x ratio at $NO_x/NH_3=0.9$. It can clearly be seen that only at an NO_2/NO_x ratio of 0.5 are nitrogen oxide conversions of about 90% achieved over the entire temperature range from 200 to 500° C. The greatest influence of the NO_2/NO_x ratio is observed in the low-temperature range up to 250° C. If little or no NO_2 is present in the test gas introduced, as is usually the case for raw exhaust gas, virtually no conversions are observed below 200° C. On the other hand, if the NO_x consists entirely of NO_2, high conversions are achieved at 250° C., but analysis of the exhaust gas downstream of the catalyst shows that the reduction of significant amounts of NO_2 does not lead to nonpolluting nitrogen but to laughing gas N_2O. Optimal conversions commencing at 75% conversion at as low as 150° C. with simultaneous optimal selectivity to nitrogen are achieved according to the stoichiometry of the reaction equation

$$2NH_3+NO+NO_2\rightarrow 2N_2+3H_2O$$

only at an NO_2/NO_x ratio of 0.5. This applies not only to SCR catalysts based on iron-exchanged zeolites but to all conventional, i.e. commercially available, SCR catalysts. However, as stated above, only small amounts of NO_2 are present in the primary exhaust gas from lean-burn engines. The ratio of NO_2 to total NO_x here is significantly less than 0.5.

[0008] At present, a combination of various exhaust gas purification units is indispensable in order to meet the forthcoming legal obligations. An apparatus for the purification of lean-burn engine exhaust gases should therefore comprise an oxidation-active catalyst and, for the removal of nitrogen oxides, an SCR catalyst with upstream metering facility for reducing agent (preferably ammonia or urea solution) and external reducing agent source (for example an additional tank containing appropriate aqueous solutions). If optimization of the combustion in the engine is not able to keep the particle emissions sufficiently low for them to be able to be removed over the oxidation catalyst by direct oxidation by means of oxygen, the additional use of a particle filter is possible.

[0009] EP1054722 describes a system for the treatment of NO_x- and particle-containing lean-burn exhaust gases from an internal combustion engine, in which an oxidation catalyst is located upstream of a particle filter. A reducing agent source and a metering facility for the reducing agent and also an SCR catalyst are arranged downstream of the particle filter. In the process described here, the proportion of NO_2 in the exhaust gas and thus the NO_2/NO_x ratio is increased by at least partial oxidation of NO over the oxidation catalyst, with the NO/NO_2 ratio preferably being "set to a predetermined level which is optimal for the SCR catalyst" (cf. claim **11** of the patent text). However, this optimal level mentioned is achieved only to an unsatisfactory extent in the process described here.

[0010] In particular, the degree of conversion of NO into NO_2 upstream of the SCR catalyst is determined by the type of oxidatively active catalyst itself, its state of aging, the exhaust gas temperature and the oxygen partial pressure in the raw emission. The latter two parameters determine the position of the equilibrium of the oxidation reaction and thus the maximum NO_2/NO_x ratio which can be achieved. Composition and state of aging of the oxidation catalyst determine the minimum exhaust gas temperature at which the activation energy necessary for the oxidation reaction is overcome by means of the catalyst and the catalyst "lights off", namely the light-off temperature of the catalyst. FIG. **2** shows by way of example the relationship between exhaust gas temperature and the NO_2/NO_x ratio established in a model gas over a conventional, platinum-containing oxidation catalyst at an oxygen content of 6% by volume. The continuous line shows the position of the equilibrium of the oxidation reaction as a function of temperature. At low temperatures up to just below 200° C., the equilibrium is completely on the side of NO_2 formation. Above 700° C., NO_2 is no longer stable and only NO is now present. The NO_2/NO_x ratio passes through 0.5 at about 400° C. The curve shown by the measurement points shows the molar NO_2/NO_x ratios actually established in a component-reduced model gas over a freshly prepared, conventional, platinum-containing oxidation catalyst. The catalyst "lights off" only at about 140° C. The degree of formation of NO_2 then increases greatly with increasing temperature until the equilibrium line is reached at about 280° C. Values for an NO_2/NO_x ratio of 0.5 are achieved above about 160° C. and are virtually immediately exceeded. Thermal aging of the catalyst and the presence of other oxidizing exhaust gas components lead to an increase in the NO light-off temperature with a simultaneous decrease in the oxidation activity. As aging increases, the equilibrium curve is reached only at ever higher exhaust gas temperatures. When the catalyst is severely aged, conversions of 50% in the NO oxidation and thus NO_2/NO_x ratios of 0.5 are sometimes no longer observed. FIG. **2** thus makes it clear how difficult ensuring an optimal NO_2/NO_x ratio is when it is set purely "passively" by means of an oxidation catalyst which is not regulated further.

[0011] It is common to all the exhaust gas purification systems for engine exhaust gases that the exhaust gas purification units are coupled to one another and to the respective operating state of the engine both thermally and chemically, i.e. based on the composition of the exhaust gas. The operating state of the engine fixes the composition of the raw exhaust gas and thus the amount of the oxidant and reducing agent available in the exhaust gas and also substantially determines the temperature of the downstream catalysts. The efficiency of the exhaust gas purification units themselves therefore depends critically on the continually changing operating point of the engine. Further parameters influencing the NO_2/NO_x ratio occur when the exhaust gas purification system additionally contains, as in EP-B-1054722, exhaust gas purification units, for example a particle filter, between oxidation catalyst and SCR stage. In this case, NO_2 is consumed during passage of the exhaust gas through the particle filter if the filter is at least partly laden with soot. The strong oxidant NO_2 then reacts with soot to form CO or CO_2 and NO, so that the NO_2/NO_x ratio is reduced again. This occurrence is also known to those skilled in the art as the "CRT effect" (CRT®=Continuous Regenerating Trap). The degree to which the NO_2/NO_x ratio is reduced depends on the state of loading of the particle filter, the NO_2 content of the exhaust gas and the exhaust gas temperature. In such a system arrangement, supply of NO_2 to the SCR stage in accordance with requirements can no longer be ensured for all operating points of the engine and over the entire operation time of the motor vehicle.

[0012] In summary, it can be seen that the concentration of NO_2 in the exhaust gas in the systems of the prior art (e.g. EP-B-1054722) depends, inter alia, on the variable particle loading of the particle filter, on the operating point of the engine, the exhaust gas temperature and the composition of the raw exhaust gas and is also influenced by geometry, type, number and activity of the exhaust gas purification units installed upstream of the SCR stage. Owing to the many influencing parameters, conditions so optimal that the abovementioned preferred NO_2/NO_x ratio of 0.5 is present upstream of the SCR catalyst can prevail only comparatively rarely over the entire driving spectrum for a fixed design of the components of the system.

[0013] In addition, it is to be expected that future engine concepts will be optimized to achieve a lower fuel consumption. This means that the efficiency of the engines will be improved further, as a consequence of which the average exhaust gas temperatures both of diesel engines and of spark-ignition engines operated under lean conditions will be reduced further. As FIG. **1** shows, the degree of conversion of NO_x over the SCR catalyst at low exhaust gas temperatures in the range from 150 to 300° C. is determined decisively by the NO_2/NO_x ratio.

[0014] It was therefore an object of the present invention to provide a process and an exhaust gas purification apparatus which helped to overcome the disadvantageous influences just outlined in the prior art. The proposed process or the abovementioned apparatuses should be at least not significantly inferior in terms of the other relevant properties to the processes and apparatuses of the prior art. In particular, the process of the invention and the apparatus should make it possible to guarantee a significantly reduced NO_x emission over a greater range of the driving spectrum and thus reduce the total emission of pollutants while continuing to achieve good values for the particle or HC and CO emission.

[0015] These objects and further objects which are not mentioned in greater detail but can be derived in an obvious manner from the prior art are achieved by a process described by the features of the present claim **1** or the use of an apparatus having the features of claim **14**.

[0016] As a result of, in a process for purifying NO_x-containing exhaust gases from a combustion process, the exhaust gases being treated by means of the following apparatuses in the order indicated:

a) by means of an oxidatively active particle filter (**1**),

b) by means of an oxidation catalyst (**2**) and

c) after addition of a sufficient amount of a reducing agent from a reducing agent source (**3***a*) via a metering facility (**3***b*), by means of an SCR catalyst (**3***c*),

with the oxidation catalyst (**2**) or its coating comprising the metals platinum or palladium or mixtures thereof, the stated object is achieved in a completely surprising and very simple but nonobvious fashion. The simple change in the arrangement of the purification units (**1**) and (**2**) compared to the prior art rules out the influence of the change in the NO_2/NO_x ratio due to the degree of loading of the particle filter (**1**) with soot. The oxidation catalyst (**2**) downstream of the particle filter (**1**) guarantees a virtually optimal ratio of NO_2/NO_x upstream of the SCR catalyst over a wide range regardless of the degree of loading of the particle filter (**1**), which appears particularly advantageous in respect of the NO_x emission. The arrangement of the oxidation catalyst (**2**) downstream of the particle filter (**1**) also brings the advantage that inorganic poisoning elements such as oil ash additives are deposited in the upstream particle filter (**1**) and do not have an adverse effect on the activity of the downstream oxidation catalyst (**1**). Despite the rearrangement of the apparatuses used compared to the proposal of the prior art (in particular EP-B-1054722), there are at least no significant deteriorations in respect of the production of other relevant pollutants.

[0017] As indicated, the exhaust gases to be purified originate from a combustion process. A person skilled in the art will be aware of the combustion processes which can come into question here. Mention may be made by way of example of processes for smelting, waste incineration, combustion of coal, etc. However, the process of the invention is advantageous for the purification of automobile exhaust gases. This refers particularly to the purification of exhaust gases from a combustion process in a lean-burn engine. A lean-burn engine is an internal combustion engine whose air-fuel mixture is kept in the lean range, in particular a diesel engine or a spark-ignition engine operated under lean conditions with direct fuel injection. Lean means that there is more combustion air present than is required for stoichiometric combustion of the fuel in the cylinder. The excess of air leads to the combustion temperature and as a result the concentration of nitrogen oxides in the exhaust gas being reduced. The combustion air ratio λ (lambda) is a number by means of which the composition of the mixture of air and fuel is described.

[0018] The combustion air ratio is the mass of air which is actually available for a combustion process to the minimum stoichiometric mass of air which is required for complete combustion. Lean-burn engines are engines which are operated for part of the time or predominantly in the λ range >1. The diesel engine in particular is a classical lean-burn concept which is operated with an excess of air ($1.3<\lambda<2.2$). Conventional spark-ignition engines are operated at an air ratio of about $\lambda=1$. A lambda sensor upstream of the catalyst measures the oxygen content of the exhaust gas and sends signals to the control unit of the automobile in order to control the supply of air. Modern spark-ignition engine concepts, for example direct fuel injection, allow lean-burn operation, which is associated with a fuel consumption advantage over stoichiometric concepts, over a wide load range.

[0019] Any oxidatively active particle filter (**1**) which appears to a person skilled in the art to be suitable for the present process can be employed for the purposes of the present invention. In general, the filters are constructed as described in WO0102083 under the name "Downstream Filter". Further possible embodiments of particle filters are mentioned in WO2006021336. The oxidative action of the particle filter (**1**) refers to the oxidizable constituents of the exhaust gas flowing through the particle filter being oxidized in the presence of the available oxygen. In this way, hydrocarbons and carbon monoxide and also NO present can be converted at least partly into CO_2, H_2O or NO_2. The oxidatively active particle filter (**1**) has the primary task of filtering out both relatively large and relatively small soot particles from the exhaust gas. The filter therefore has to be freed of the soot particles at appropriate times so as not to become blocked. This is achieved by oxidation of the soot particles collected in the filter by means of the oxygen present or by NO_2 formed by the oxidatively active filter (**1**) itself (CRT® effect) in the exhaust gas. The above-described oxidation of the particles in the particle filter (**1**) can thus be effected either continuously (e.g. by means of the above-described CRT® effect) or discontinuously by increasing the exhaust gas temperature. Temperatures which lead to rapid burn-off of the soot collected in the particle filter, also known as regeneration of the particle filter, are normally about 600° C. These high temperatures are usually achieved only by additional heating measures such as after-injection of fuel, which is associated with an increase in fuel consumption. The closer the particle filter (**1**) is arranged to the engine space, the higher the average temperature of the exhaust gases and the more easily can the temperature required for burning-off of soot be achieved.

[0020] The oxidation of these soot particles is aided further by the filter (**1**) itself having an oxidative action. This can be brought about by this filter containing catalytically active components. These can be located either in the filter or on the filter surface. An advantageous embodiment is one in which the particle filter (**1**) as mentioned above is additionally coated with an oxidatively active catalyst. This firstly reduces the light-off temperature for combustion of the soot on the coated filter and secondly enables the desired CRT® effect to be advantageously displayed.

[0021] As catalytically active components or coatings, it is possible for a person skilled in the art to use, for example, those described in PCT/EP2008/000631 or in the doctoral thesis by Stephan Liebsch, TU Dresden 2004. The particle filter (**1**) and in particular the coating mentioned preferably comprises metals such as platinum, palladium, rhodium or mixtures thereof, which are then advantageously applied to high-surface-area support materials. Greater preference is given to using platinum-palladium mixtures. A person skilled in the art will select the appropriate mixing ratio of the metals, if appropriate as a function of the proportion of oxidizing species in the exhaust gas and the temperature regime to be adhered to. The oxidatively active coating or the particle filter (**1**) can preferably have a molar ratio of platinum to palladium in the range from 15:1 to 1:3, in particular from 15:1 to 5:1.

[0022] Particularly in the case of spark-ignition engines operated under lean conditions, it may also appear to be useful to apply catalysts having a 3-way function, which give high degrees of conversion of hydrocarbons, carbon monoxide and nitrogen oxides under both lean and stoichiometric exhaust gas conditions, as catalytically active coatings. The mode of operation and appropriate design of 3-way catalysts is comprehensively described in, for example, EP1046423 and WO95/35152.

[0023] In a further embodiment of the invention, the catalytic coating of the particle filter (**1**) can also have the function of storing nitrogen oxides and/or oxygen under lean-burn exhaust gas conditions. The advantage of such an NO_x storage function (NSC—NO_x Storage Catalyst) or an oxygen storage function (OSC—Oxygen Storage Catalyst) of the component (**1**) is that the nitrogen oxides present in the exhaust gas can be filtered out even at low exhaust gas temperatures at which the downstream SCR catalyst is not yet active and can be desorbed from the storage centers at higher temperatures at which SCR operation is possible and reacted over the downstream SCR system (as described in WO2004076829). Basic oxides, carbonates or hydroxides of alkali metals, alkaline earth metals and rare earth metals, in particular basic compounds of barium and strontium and also of cerium, are employed for the storage of nitrogen oxides as nitrates. The NO_x storage preferably comprises components selected from among the oxides of cerium, barium and strontium and mixtures thereof.

[0024] The oxidation catalyst (**2**) can likewise be configured as required by a person skilled in the art as long as it or its coating comprises the metals platinum or palladium or mixtures thereof. Preference is given to the oxidation catalyst (**2**) not containing any further noble metals apart from platinum, palladium or mixtures thereof. In particular, the oxidation catalyst (**2**) should not contain any rhodium. The oxidation catalyst should advantageously have no further functions such as an NOx storage function, three-way function or oxygen storage function. Very particular preference is given to the oxidation catalyst (**2**) not performing an NOx storage function. Suitable embodiments can be found in the patent applications DE10308288, DE19614540, DE19753738, DE3940758, EP427970, DE 4435073. It is possible to use, for example, conventional oxidation catalysts (**2**) having an oxidatively active catalyst coating on a support material. The oxidation catalyst (**2**) and in particular the catalyst coating can preferably have a molar ratio of platinum to palladium in the range from 15:1 to 1:3, in particular from 15:1 to 5:1. Examples of oxidatively active catalyst coatings may also be found in the abovementioned patent applications.

[0025] As regards suitable support materials for use in the abovementioned particle filter (**1**) or oxidation catalyst (**2**), reference may be made to EP 0800856. There and in the documents cited there, suitable supports are likewise described. The support described there comprises a zeolite mixture composed of a plurality of zeolites having different moduli and platinum group metals and also further metal oxides from the group consisting of aluminum silicate, aluminum oxide and titanium oxide, with the aluminum silicate having a weight ratio of silicon dioxide/aluminum oxide of from 0.005 to 1, preferably from 0.01 to 0.5, particularly preferably from 0.05 to 0.1, and the platinum group metals advantageously being able to be deposited only on the further metal oxides. In a preferred embodiment, the catalyst contains platinum on an aluminum silicate and also up to five different zeolites. The zeolites can be selected from the group consisting of mordenite, H-ZSM5, Na-ZSM5, Y-zeolite, dealuminated Y-zeolite (DAY) and β-zeolite. The concentration of the platinum group metals on the oxidic support materials can here be in the range from 0.1 to 5% by weight based on the support material. Preference is given to a range of 0.5-4% by weight and particularly preferably 1.5-3.8% by weight.

[0026] A further example in this context is U.S. Pat. No. 6,767,855. There and in the documents cited there, single-layer and multilayer catalysts which contain zeolites as hydrocarbon-absorbing material and also catalytically active noble metals of the platinum group (platinum, palladium, rhodium, iridium and ruthenium) which are preferably deposited on aluminum oxide are described. The hydrocarbon-absorbing zeolites are preferably located in a separate layer which is applied directly to a support body. The zeolites can be coated with noble metals such as palladium or silver. The further catalyst layers are applied on top of this absorbing layer and can comprise a cerium-containing oxide in addition to the aluminum oxide activated with the platinum group metals. U.S. Pat. No. 6,756,336 describes, as does U.S. Pat. No. 6,767,855, (both of which are incorporated by reference) single-layer and multilayer catalysts which contain zeolites as hydrocarbon-absorbing materials and are suitable for the purposes of the invention.

[0027] After the exhaust gas has been treated with the oxidation catalyst (**2**), a ratio of NO_2/NO_x which is essentially independent of the properties of the particle filter (**1**) prevails in the exhaust gas. A significant source of influence on the NO_2/NO_x ratio is therefore eliminated, which astonishingly makes it possible to keep this ratio more readily within preferred ranges. A significant further control parameter for the stated NO_2/NO_x ratio is, apart from the temperature in the oxidation of the exhaust gases over the oxidation catalyst (**2**) at which NO is oxidized to NO_2 and CO and HC components are also oxidized to CO_2 and H_2O, the oxygen content of the exhaust gas. This parameter can, if appropriate, be predetermined in a targeted manner by the electronically controlled engine control system. Thus, it is possible to set the oxygen content in the exhaust gas in a control circuit as a function of the temperature prevailing at the oxidation catalyst (**2**). The amount of oxygen present in the exhaust gas is therefore preferably regulated so that the molar NO_2/NO_x ratio upstream of the SCR catalyst (**3***c*) is increased to values of from about 0.3 to 0.7, if possible independently of the temperature of the oxidation catalyst (**2**). Particular preference is given to setting a range from about 0.4 to 0.6, very particularly preferably a value of from about 0.45 to 0.55.

[0028] To minimize the temperature dependence in this range further, it can be useful to subject the oxidation catalyst (**2**) to heat treatment so that a uniform temperature can be set over various operating points of the engine, which in turn leads to a more uniform and therefore more easily reduced NO_2/NO_x ratio. The temperature set in the oxidation catalyst (**2**) is preferably 200° C.-500° C., more preferably 250-400° C. and particularly preferably 300° C.-350° C. The heat treatment can be carried out by methods known to those skilled in the art, for example by means of engine measures such as after-injection and throttling for heating or dethrottling and increased exhaust gas recirculation for cooling and also by electric heating or cooling by means of heat exchangers.

[0029] A reducing agent is subsequently introduced into the exhaust gas which has been treated in this way. As reducing agents, it is possible to employ all agents which a person skilled in the art would consider for this purpose. In particular, the use of aqueous solutions of ammonia, urea or ammonium carbamate, ammonium nitrate or other materials which liberate ammonia under the given conditions is possible here.

These can be taken from a reservoir (3*a*) which is known per se to those skilled in the art and added to the exhaust gas stream in a suitable way. The addition can be effected by means of apparatuses known to those skilled in the art. The optimal ratio of $NH_3/NO_2—NO_x$ (EP1054722) is set by means of these so that very complete conversion of the nitrogen oxides into N_2 can occur.

[0030] This reaction just mentioned can be carried out over SCR catalysts (**3***c*) known to those skilled in the art. Nitrogen oxides are converted in a selective fashion into nonhazardous nitrogen over these catalysts under reducing conditions. Suitable SCR catalysts and apparatuses are described by way of example in DE10308288, EP385164, U.S. Pat. No. 4,961, 917, EP1495804, EP1147801 and U.S. Pat. No. 7,005,116 or U.S. Pat. No. 6,914,026. In this context, particular preference is given to iron- or copper-exchanged zeolites or preferably transition metal-exchanged zeolites and/or materials in which transition metal oxides selected from the group consisting of vanadium pentoxide, tungsten trioxide and titanium dioxide are present. As transition metal present in the zeolite, preference is given to using a metal selected from the group consisting of copper, manganese, cobalt, nickel, silver and gold or combinations thereof. Very particular preference is given to using copper in this context.

[0031] As further alternatives, the SCR catalyst can comprise titanium dioxide, zirconium dioxide, compounds of tin, molybdenum, niobium, cerium or combinations of these components.

[0032] An advantageous embodiment is likewise one in which an NO_x storage catalyst as described above is installed upstream of the SCR catalyst (**3***c*).

[0033] A further invention leading to achievement of the objects mentioned is the provision of an exhaust gas purification apparatus comprising, in the following order moving away from the combustion process:

[0034] a) an oxidatively active particle filter (**1**)

[0035] b) an oxidation catalyst (**2**) and

[0036] c) an SCR stage (**3**) comprising

[0037] (**3***a*) an external reducing agent source

[0038] (**3***b*) a metering apparatus

[0039] (**3***c*) a reduction catalyst (SCR catalyst),

with the oxidation catalyst (**2**) or its coating comprising the metals platinum or palladium or mixtures thereof.

[0040] The abovementioned process can be carried out advantageously using such an apparatus. The definitions and explanations and also preferred embodiments described for the process of the invention apply analogously to the exhaust gas purification apparatus of the invention in terms of the physical configuration.

[0041] The apparatus of the invention or the abovementioned process can be supplemented by further purification units familiar to those skilled in the art, e.g. pre-turbo catalysts (SAE preliminary publication 2008-01-0768) installed upstream of the system according to the invention or oxidation catalysts preventing NH_3 slip (DE 197 34 627 C1) installed downstream of the system according to the invention. Oxidation catalysts installed downstream in this way can be configured like the above-described oxidation catalysts (**2**).

[0042] The present invention has made it possible to operate an exhaust gas purification process which combines substantial advantages by means of relatively simple measures. The arrangement of the particle filter (**1**) upstream of the oxidation catalyst (**2**) minimizes the influence and thus the disturbance which this can have on the critical NO_2/NO_x ratio. When this layout is used, the oxidation catalyst (**2**) no longer has to generate sufficient heat for a filter regeneration to be able to take place, as a result of which the thermal stress on the oxidation catalyst is decreased. For this reason, the metal loading of the oxidation catalyst can be decreased or altered, which helps save noble metal costs. The emissions of CO and HCs which may occur during particle burn-off in the particle filter (**1**) necessarily pass through the downstream oxidation catalyst (**2**) on their path through the system according to the invention, which once again leads to such incompletely burnt exhaust gas components being converted into CO_2 and H_2O. A system having these advantages cannot be derived in an obvious fashion from the prior art. The fact that the advantages described are achieved by means of relatively small modifications of such an exhaust gas purification system with further improved performance of the exhaust gas purification process is all the more surprising.

EXAMPLES

[0043] The invention is illustrated below in FIGS. **1** to **3** and an example. The figures show:

[0044] FIG. **1**: dependence of the nitrogen oxide conversion and the selectivity of the reduction of nitrogen oxide over a conventional reduction catalyst based on an iron-exchanged zeolite on the molar NO_2/NO_x ratio at $\alpha=NO_x/NH_3=0.9$ and a space velocity of 30 000 L/h;

[0045] catalysts were examined in the freshly prepared state on a model gas test bench using a defined model gas composition; the curves marked by solid symbols and continuous lines show the NO_x conversion, the curves represented by the corresponding open symbols and broken lines show the respective N_2O concentrations in the exhaust gas downstream of the catalyst; in the graphs:

[0046] (•)/(○) are measured values for $NO_2/NO_x=0.5$;

[0047] (▲)/(Δ) are measured values for $NO_2/NO_x=0 \rightarrow NO_x=NO$ and

[0048] (■)/(□) are measured values for $NO_2/NO_x=1 \rightarrow NO_x=NO_2$

[0049] FIG. **2**: relationship between the exhaust gas temperature and the molar NO_2/NO_x ratio established over a conventional, platinum-containing oxidation catalyst, measured in a component-reduced model gas having an oxygen content of 6% by volume;

[0050] continuous line=calculated equilibrium position of the reaction

[0051] $NO+\frac{1}{2}O_2 \rightarrow NO_2$

[0052] (◇)=measured molar NO_2/NO_x ratio where $NO_x=NO+NO_2$ over a conventional Pt-based oxidation catalyst;

[0053] FIG. **3**: exhaust gas purification system for carrying out the process of the invention in a preferred embodiment; here, the reference numerals have the following meanings:

[0054] (**1**) oxidatively active particle filter

[0055] (**2**) oxidation catalyst

[0056] (**3**) SCR stage comprising:

[0057] (**3***a*) external reducing agent source, e.g. tank for urea solution

[0058] (**3***b*) metering apparatus, e.g. injection nozzle

[0059] (**3***c*) reduction catalyst (SCR catalyst)

DESCRIPTION OF THE STRUCTURE AND THE PROCEDURE

[0060] For the study, two systems were measured in a simulated FTP72 cycle on a model gas unit and the efficiency in respect of the oxidation of HC, CO and NO was determined. The structure of the systems examined is described below. The DOC or DPF coating technology was selected according to the layout, with the two systems being comparable from the point of view of noble metal costs. The catalyst volumes used are likewise identical. The inlet parameters for the model gas reactor (temperature, concentration of HCs, CO, NOx, NO) are taken from an engine application designed for the American regulation Tier2 Bin5. The measurements were carried out without a downstream SCR catalyst. To carry out the invention, it is possible to use conventional units for exhaust gas purification which were commercially available at the point in time of the invention. Catalysts mass-produced by Umicore which were thermally aged beforehand (cDPF: 48 hours at 800° C.; DOC: 48 hours at 750° C.) were used for the study.

System Test 1

cDPF Before DOC Before Urea-SCR—According to the Invention

[0061] As cDPF (coated diesel particulate filter), a technology having a platinum-palladium coating in a ratio of 2:1 was used in this system. The noble metal loading was 55 g/ft^3. The DOC (diesel oxidation catalyst) is an oxidation catalyst having a platinum:palladium ratio of 1:0. The noble metal loading here was 60 g/ft^3.

System Test 2

DOC Before cDPF Before Urea-SCR—Comparative Example

[0062] The DOC is an oxidation catalyst having a platinum-palladium ratio of 2:1 and a noble metal loading of 110 g/ft^3. The filter coating of the cDPF has a platinum:palladium ratio of 6:1 at a noble metal loading of 35 g/ft^3.

Discussion of Results:

[0063] The NO_x and NO inlet concentration curves are shown by way of example in FIG. **4**. Measuring the difference between the NO_x and NO curves enables the inlet concentration (before passage over a purification unit—inlet) of NO_2 to be determined. The NO_2 emission calculated for the test is shown as 0.032 g/ml in table 1 and corresponds approximately to a proportion of 16% of the incoming NO_x emission.

[0064] FIG. **5** shows the NO_2 concentration curves after System Test 1 and System Test 2. These concentration curves display higher NO_2 concentrations in System Test 1.

TABLE 1

	HC [g/mi]	CO [g/mi]	NO_x [g/mi]	NO_2 [g/mi]	NO_2/NO_x
Inlet	0.723	4.326	0.196	0.032	0.16
System Test 1	0.026	0.359	0.180	0.072	0.40
System Test 2	0.015	0.297	0.179	0.049	0.27

[0065] As can be seen from the table, there is a significant improvement in the proportion of NO_2 upstream of the SCR, which increases to almost 40% of the total NO_x. In contrast, the NO_2 content of the NO_x in Test 2 is significantly lower under otherwise identical conditions. A poorer conversion over the SCR catalyst is thus preprogrammed (G. Tuenter et al., Ind. Eng. Chem. Prod. Res. Dev. 1986, 25, 633-636). Furthermore, the HC emission (3.6% instead of 2%) and the CO emission (8.3% instead of 6.9%) increase only slightly.

1. A process for purifying NO_x-containing exhaust gases from a combustion process:

characterized in that

the exhaust gases are treated by means of the following apparatuses in the order indicated:

a) by means of an oxidatively active particle filter (**1**),

b) by means of an oxidation catalyst (**2**) and

c) after addition of a sufficient amount of a reducing agent from a reducing agent source (**3***a*) via a metering facility (**3***b*), by means of an SCR catalyst (**3***c*), with the oxidation catalyst (**2**) or its coating comprising the metals platinum or palladium or mixtures thereof.

2. The process as claimed in claim **1**,

characterized in that

the oxidation catalyst (**2**) does not contain any rhodium.

3. The process as claimed in claim **1**,

characterized in that

the oxidation catalyst (**2**) does not perform an NOx storage function.

4. The process as claimed in claim **1**,

characterized in that

the combustion process takes place in a lean-burn engine.

5. The process as claimed in claim **1**,

characterized in that

the particle filter (**1**) is coated with an oxidatively active catalyst.

6. The process as claimed in claim **1**,

characterized in that

the particle filter (**1**) or its coating comprises the metals platinum, palladium or rhodium or mixtures thereof.

7. The process as claimed in claim **6**,

characterized in that

the particle filter (**1**) or its coating has a molar ratio of platinum to palladium in the range from 15:1 to 1:3.

8. The process as claimed in claim **1**,

characterized in that

the particle filter (**1**) is coated with a catalyst having a 3-way function.

9. The process as claimed in claim **1**,

characterized in that

the oxidation catalyst (**2**) or its coating has a molar ratio of platinum to palladium in the range from 15:1 to 1:3.

10. The process as claimed in claim **1**,

characterized in that

the particle filter (**1**) has an NO_x storage function.

11. The process as claimed in claim **10**,

characterized in that

the particle filter (**1**) contains oxides of cerium, barium or strontium or mixtures thereof as NO_x storage components.

12. The process as claimed in claim **1**,

characterized in that

the molar NO_2/NO_x ratio upstream of the SCR catalyst (**3***c*) is set to values of from about 0.3 to 0.7 by regulating the amount of oxygen present in the exhaust gas.

13. The process as claimed in claim **1**,

characterized in that

the oxidation catalyst (**2**) is heat treated.

14. An exhaust gas purification apparatus comprising, in the following order moving away from the combustion process:

a) an oxidatively active particle filter (**1**)
b) an oxidation catalyst (**2**) and
c) an SCR stage (**3**) comprising
  (**3***a*) an external reducing agent source
  (**3***b*) a metering apparatus
  (**3***c*) a reduction catalyst (SCR catalyst),

with the oxidation catalyst (**2**) or its coating comprising the metals platinum or palladium or mixtures thereof.

15. The exhaust gas purification apparatus as claimed in claim **14**,

characterized in that

the configuration of the apparatus corresponds to claim **2**.

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