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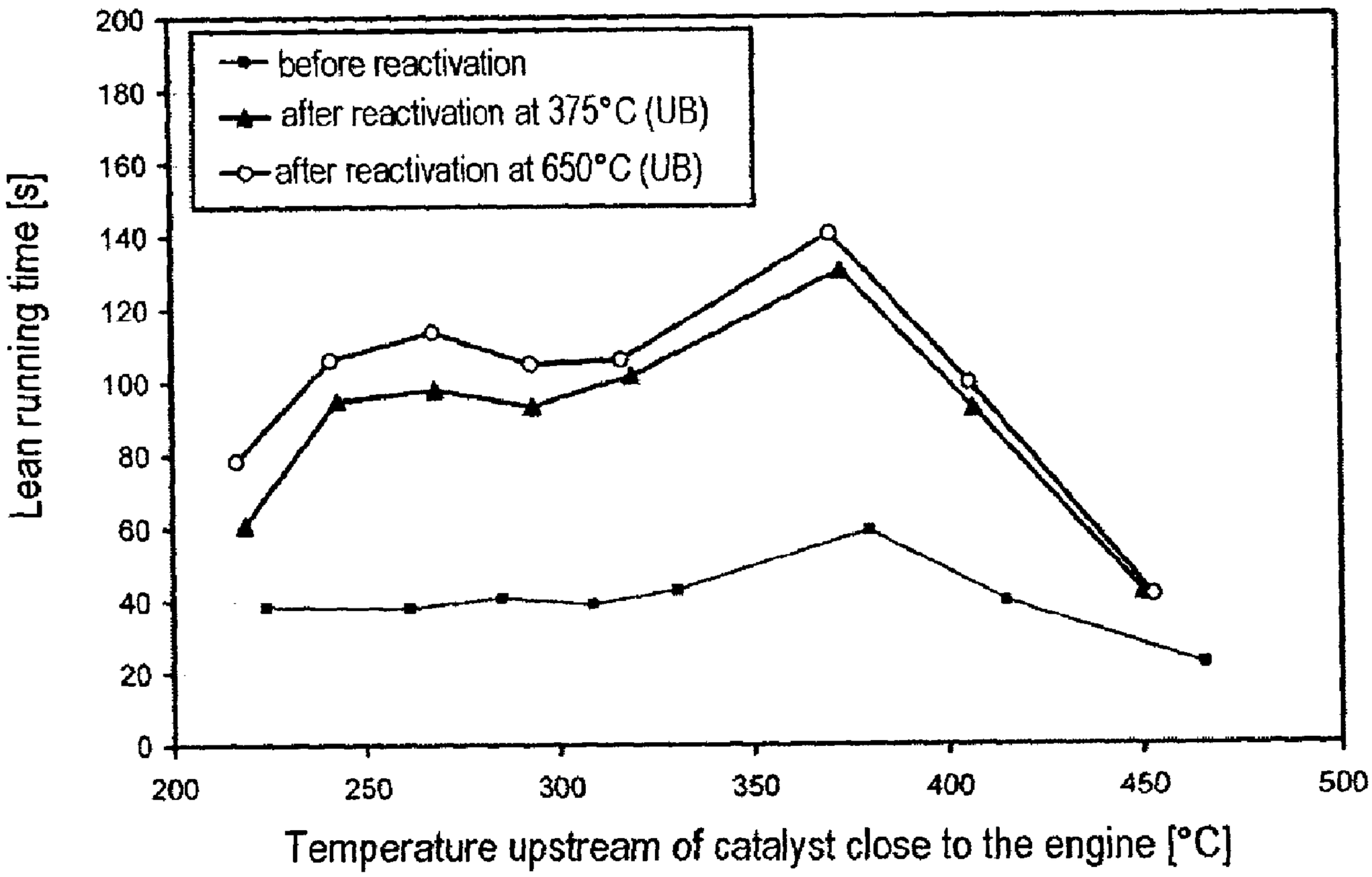
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(54) Titre : PROCEDE POUR LA REACTIVATION INTEGREE DE CATALYSEURS A ACCUMULATION D'OXYDES D'AZOTE THERMIQUEMENT VIEILLIS DANS DES VEHICULES AUTOMOBILES A MOTEUR A COMBUSTION INTERNE FONCTIONNANT PRINCIPALEMENT AVEC UN MELANGE PAUVRE

(54) Title: METHOD FOR THE ON-BOARD REACTIVATION OF THERMALLY AGED NITROGEN OXIDE STORAGE CATALYSTS IN MOTOR VEHICLES HAVING AN INTERNAL COMBUSTION ENGINE OPERATED PREDOMINANTLY UNDER LEAN CONDITIONS



(57) Abrégé/Abstract:
Nitrogen oxide storage catalysts are used for removal of nitrogen oxides present in the lean exhaust gas of so-called lean-burn engines. Storage catalysts are thermally modified at high temperatures. The modification is a sintering of the catalytically active

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(57) Abrégé(suite)/Abstract(continued):
noble metal components of the catalyst and a formation of compounds of the storage components with the support materials. According to the invention, the formation of compounds of the storage materials can be largely reversed by treatment of the storage material with a gas mixture containing carbon dioxide, optionally steam and optionally nitrogen oxide at temperatures between 200 °C and 950 °C, preferably between 300 °C and 700 °C. The reactivation can be carried out with neutral emissions directly in the vehicle during operation by the adjustment of suitable exhaust conditions and regulating the fuel/air mixture.

Abstract

Nitrogen oxide storage catalysts are used to remove the nitrogen oxides present in the lean exhaust gas of lean-burn engines. Storage catalysts are thermally aged by high temperatures. Ageing is due to sintering of the catalytically active noble metal components of the catalyst and to formation of compounds of the storage components with the support materials. According to the invention, the formation of compounds of the storage materials can be largely reversed by treatment of the storage material with a gas mixture containing carbon dioxide, optionally water vapor and optionally nitrogen oxides at temperatures in the range from 200°C to 950°C, preferably from 300°C to 700°C. The reactivation can be carried out under emission-neutral conditions directly in the vehicle during driving operation by setting of suitable exhaust gas conditions and regulating the air/fuel ratio.

Method for the on-board reactivation of thermally aged nitrogen oxide storage catalysts in motor vehicles having an internal combustion engine operated predominantly under lean conditions

Description

The invention relates to a method for the reactivation of thermally aged nitrogen oxide storage catalysts comprising compounds which store nitrogen oxides on a support material comprising cerium oxide in motor vehicles having internal combustion engines operated predominantly under lean conditions during operation of the vehicle.

Nitrogen oxide storage catalysts are used for removing the nitrogen oxides present in the lean exhaust gas of lean-burn engines. Here, the purifying action is based on the nitrogen oxides being stored predominantly in the form of nitrates by the storage material of the storage catalyst in a lean operating phase of the engine and the previously formed nitrates being decomposed and the nitrogen oxides which have been liberated again being reacted with the reducing components of the exhaust gas over the storage catalyst to form nitrogen, carbon dioxide and water in a subsequent rich operating phase of the engine. For the purposes of the present invention, lean-burn engines include petrol and diesel engines which are operated using a lean air/fuel mixture during most of their time of operation and can be operated in an emission-neutral fashion using a stoichiometric air/fuel mixture. The nitrogen oxides present in the exhaust gas of these engines during the lean phases comprise mostly nitrogen monoxide.

The mode of operation of nitrogen oxide storage catalysts is comprehensively described in the SAE document SAE 950809. According to this, nitrogen oxide storage catalysts comprise a catalyst material which is usually applied in the form of a coating to a support body. The catalyst material contains a nitrogen oxide storage material and a catalytically active component. The nitrogen oxide storage material in turn comprises the actual nitrogen oxide storage component which has been deposited in finely divided form on a support material.

As storage components, use is made predominantly of the basic oxides of the alkali metals, the alkaline earth metals and the rare earth metals, in particular strontium oxide and barium oxide, which react with nitrogen dioxide to form the corresponding nitrates. It is known that these materials are mostly present in the form of carbonates and hydroxides in air. These compounds are likewise suitable for storing the nitrogen

oxides. When reference is made, in the context of the invention, to the basic storage oxides, the corresponding carbonates and hydroxides are therefore also included.

Suitable storage materials for the storage components are thermally stable metal oxides which have a high surface area of more than 10 m^2/g and make deposition of finely divided storage components possible. The present invention is concerned, in particular, with storage materials which comprise support materials containing cerium oxide. These include doped cerium oxide and in particular the mixed oxides of cerium with zirconium.

As catalytically active components, use is made of the noble metals of the platinum group which are generally deposited separately from the storage components on a separate support material. As support material for the platinum group metals, use is made predominantly of an active, high-surface-area aluminum oxide which can likewise contain doping components.

The task of the catalytically active components is to convert carbon monoxide and hydrocarbons in the lean exhaust gas into carbon dioxide and water. In addition, they should oxidize the nitrogen monoxide present in the exhaust gas to nitrogen dioxide so that it can react with the basic storage material to form nitrates. As increasing amounts of nitrogen oxides are incorporated into the storage material, the storage capacity of the material decreases. Regeneration of the storage material therefore has to be carried out from time to time. For this purpose, the engine is operated using rich air/fuel mixtures for a short time. Under the reducing conditions in the rich exhaust gas, the nitrates formed are decomposed into nitrogen oxides and reduced to nitrogen using carbon monoxide, hydrogen and hydrocarbons as reducing agents, forming water and carbon dioxide.

Storage catalysts are subjected to high exhaust gas temperatures for part of the time during operation, which can lead to thermal damage to the catalysts. A distinction can be made between two significant ageing effects:

- The catalytically active noble metal components are present in finely divided form having average particle sizes in the range from about 2 to 15 nm on the oxidic materials of the storage catalyst. Owing to the small particle size, the noble metal particles have a high surface area for interaction with the constituents of the exhaust gas. Particularly in the case of lean exhaust gas of lean-burn engines, an irreversible enlargement of the noble metal crystallites, which is associated with an irreversible

reduction in the catalytic activity, is observed with increasing exhaust gas temperature.

- The storage components are likewise subjected to sintering, which likewise reduces their catalytically active surface area, at high temperatures. In addition, it has been observed that the storage components deposited on support materials react with the support materials at high temperatures to form compounds which have a relatively low storage capacity for nitrogen oxides (see SAE Technical Paper 970746 and EP 0982066 A1). If, for example, barium oxide is used as storage component on a support material containing cerium oxide, there is a risk of barium cerate ($BaCeO_3$) being formed.

The sintering of the noble metal particles is an irreversible process. Restoration of the original crystallite sizes by means of a specific treatment does not appear to be possible. On the other hand, the formation of compounds between storage components and support materials can, subject to particular prerequisites, be reversed again by means of a suitable treatment and catalytic activity of a nitrogen oxide storage catalyst can in this way at least be partly restored after thermal damage. Since the nitrogen oxide storage catalyst is typically a constituent of a fixed exhaust gas purification unit which is installed in a motor vehicle and can only be removed with considerable effort, it is of considerable importance for the practical utility of a catalyst reactivation method for the conditions required for reactivation to be able to be set during driving operation and be able to be made emission-neutral.

It is therefore an object of the present invention to provide a method for the reactivation of nitrogen oxide storage catalysts whose storage capacity has been reduced by formation of compounds by reaction of the storage components with the support materials as a result of high temperatures during normal driving operation of a motor vehicle having an internal combustion engine operated predominantly under lean conditions. Here, it also has to be ensured during the reactivation phases that the applicable emission limit values are largely adhered to.

This object is achieved by a method for on-board reactivation of a thermally aged nitrogen oxide storage catalyst, where the storage catalyst comprises basic strontium or barium compounds or strontium and barium compounds on a support material containing cerium oxide and additionally contains strontium and/or barium compounds with the support material formed by the thermal ageing. In the process, the compounds of strontium and/or barium with the support material are decomposed by treatment with

a gas mixture which contains carbon dioxide, optionally water and optionally nitrogen oxides during normal driving operation of a motor vehicle having an internal combustion engine operated predominantly under lean conditions. The gas mixture is generated by the engine of the vehicle, and the air index of the gas mixture during the decomposition process does not exceed $\lambda = 1$. If appropriate, the air index of the gas mixture produced by the engine can be adjusted by introduction of a reducing agent directly into the exhaust gas train upstream of the catalyst.

The invention makes use first and foremost of the decomposition reactions of barium cerate in an atmosphere containing carbon dioxide.

In Appl. Catal. B 63 (2005) 232 – 242, CASAPU et al. state that, according to X-ray studies, $BaCeO_3$ in $Pt/BaCeO_3$-BaO/CeO_2 decomposes to form barium carbonate $BaCO_3$ and cerium oxide after heating to 950°C in an atmosphere comprising 20% by volume of CO_2 in helium. Furthermore, they present thermoanalytic studies according to which weight changes occur in a $Pt/BaCeO_3$-BaO/CeO_2 sample in the temperature range from 400°C to 980°C when the sample is heated in an atmosphere comprising 20% by volume of CO_2 in helium and attribute the weight changes observed to the decomposition of barium cerate and the reaction of barium oxide with carbon dioxide. In another place in the same publication, it is stated that barium cerate is decomposed more slowly at 300°C in an atmosphere of about 3% of water in helium which is free of nitrogen dioxide than in the presence of nitrogen dioxide, although a significant amount of the barium cerate is said to be decomposed even without nitrogen dioxide after a reaction time of 5 hours.

Barium cerate can thus be decomposed in the presence of carbon dioxide at temperatures above 400°C. This proceeds by a two-stage reaction mechanism according to equation (1).

$$BaCeO_3 \rightarrow \left.\begin{array}{l} BaO + CeO_2 \\ \downarrow CO_2(g) \\ BaCO_3 \end{array}\right\} \quad (1)$$

If the gas mixture additionally contains water vapor, the decomposition of barium cerate commences at 300°C, with a two-stage reaction mechanism (2) likewise being able to be assumed.

$$BaCeO_3 + H_2O(g) \rightarrow \left.\begin{array}{l} BaO + CeO_2 + H_2O(g)\uparrow \\ \downarrow CO_2(g) \\ BaCO_3 \end{array}\right\} \quad (2)$$

Accordingly, it is advantageous for the exhaust gas used for reactivation to contain not only a high proportion of carbon dioxide but also significant amounts of water. Nitrogen dioxide may likewise be present. The exhaust gas used for reactivation preferably contains from 5 to 20% by volume of carbon dioxide and also from 5 to 15% by volume of water vapor and from 0 to 5% by volume of nitrogen dioxide.

Since the object of the invention is to reactivate a thermally aged nitrogen oxide storage catalyst during normal driving operation, the emission neutrality of the vehicle has to be ensured during catalyst reactivation, too. This means that the concentrations of the exhaust gas components emitted from the vehicle must not exceed the legally prescribed emission limit values during reactivation of the nitrogen oxide storage catalyst.

The inventive solution of the problem is to reactivate the nitrogen oxide storage catalyst by setting an air/fuel ratio for operation of the engine such that the exhaust gas used for reactivation has an air index which does not exceed $\lambda = 1$. Preference is given to setting an air index of $\lambda = 1$, where $\lambda = 1$ means, for the purposes of the present text, that an oscillating change between a slightly higher and a slightly lower air index occurs in such a way that an average air index of $\lambda = 1$ is maintained. The air index range in which such an oscillation occurs is from $\lambda = 0.9$ to $\lambda = 1.1$, preferably from $\lambda = 0.95$ to $\lambda = 1.05$ and very particularly preferably from $\lambda = 0.98$ to $\lambda = 1.02$, as is customary for operation of a three-way catalyst.

Such a choice of engine operation ensures that the exhaust gas mixture produced and required for reactivation contains sufficiently large amounts of carbon dioxide and water for reactivation when passed over the nitrogen oxide storage catalyst. This is particularly the case when the exhaust gas purification unit used in the vehicle contains two exhaust gas purification converters, namely a catalytic converter close to the engine and an underbody converter. Both converters can contain nitrogen oxide storage catalysts. As an alternative, the converter close to the engine can contain a three-way catalyst or a diesel oxidation catalyst and the underbody converter can have a nitrogen oxide storage catalyst. Both the nitrogen oxide storage catalyst used close to the engine, which as described contains a catalytically active noble metal component whose task is to convert carbon monoxide and hydrocarbons into carbon dioxide and water by means of the oxygen present in the exhaust gas, and also the three-way catalyst or the diesel

oxidation catalyst ensure an increase in the carbon dioxide concentration and the water concentration in the exhaust gas. A gas mixture which is well-suited to the reactivation of the nitrogen oxide storage catalysts is thus made available and emission neutrality is at the same time guaranteed.

Modern internal combustion engines operated under lean conditions with a jet-controlled combustion process can under certain conditions be operated using a superstoichiometric air/fuel ratio and air indices of $\lambda > 1$ even at operating points with vehicle speeds in the range from 120 to 150 km/h, which are already outside the European driving cycle. Such a mode of operation is in principle preferred if higher fuel savings are to be achieved. However, if the nitrogen oxide storage catalyst has lost some of its storage capacity as a result of thermal ageing, the breakthrough of nitrogen oxides has to be avoided by more frequent switching over to a substoichiometric air/fuel ratio (rich operation), with the fuel consumption advantage over stoichiometric air/fuel operation being lost at an air index of $\lambda = 1$. Operating points with a stoichiometric air/fuel ratio can thus be utilized for reactivating the nitrogen oxide storage catalyst without increased fuel consumption compared to further operation of a thermally aged nitrogen oxide storage catalyst which has not been reactivated.

Since a time of at least a few minutes is necessary for the reactivation according to the invention of the nitrogen oxide storage catalyst, it is advantageous to choose phases of driving operation in which the vehicle is operated at speeds above 100 km/h for at least a few minutes for reactivation of the catalyst. According to the invention, a stoichiometric air/fuel ratio is set and a thermally aged nitrogen oxide storage catalyst is reactivated at such operating points. Under these conditions, exhaust gas temperatures of from 200°C to 950°C are generated and these are well-suited for the decomposition reaction of barium cerate in an atmosphere containing carbon dioxide. Preference is given to temperatures in the range from 300°C to 700°C, very particularly preferably from 400°C to 650°C.

The desulfurization of nitrogen oxide storage catalysts is frequently carried out at an oscillating air index of the exhaust gas in the range from $\lambda = 0.8$ to $\lambda = 1.1$. The reactivation of a thermally aged nitrogen oxide storage catalyst can also be coupled with such a desulfurization procedure. However, this is not necessary. Desulfurizations are usually started at catalyst temperatures above 600°C. The reactivation of the thermally aged nitrogen oxide storage catalyst, on the other hand, is possible at temperatures from 200°C and temperatures in the range from 400°C to 650°C are particularly preferred. Cooler operating points independent of the desulfurization are thus significantly more

advantageous, especially since other thermal ageing effects, for example on the noble metal component, are avoided at lower temperatures.

Under the operating conditions mentioned, the required emission neutrality can be ensured at any time when an exhaust gas purification unit which contains a nitrogen oxide storage catalyst in a converter in the underbody position and in a converter close to the engine or alternatively has a nitrogen oxide storage catalyst in a converter in the underbody position and a three-way catalyst in a converter close to the engine is used. Both embodiments ensure that sufficient conversions of carbon monoxide, hydrocarbons and nitrogen oxides are obtained at an engine operating point using a stoichiometric air/fuel mixture without the nitrogen oxide storage function of the nitrogen oxide storage catalyst to be reactivated having to be utilized.

In a further embodiment of the invention, the reactivation of a nitrogen oxide storage catalyst which has basic strontium or barium compounds or strontium and barium compounds on a support material containing cerium oxide and also strontium and/or barium compounds with the support material formed by thermal ageing can be effected even with a gas mixture having an air index $\lambda < 1$ when suitable exhaust gas temperatures are ensured. Such gas mixtures generally also contain sufficient amounts of carbon dioxide and possibly water. To guarantee emission neutrality, additional measures may then be necessary since otherwise there is a risk of, in particular, high residual hydrocarbon emissions. For this purpose, a series of modifications of the exhaust gas unit are conceivable, for example arrangement of an oxidation catalyst downstream of the nitrogen oxide storage catalyst to be reactivated, if appropriate in combination with introduction of secondary air between the nitrogen oxide storage catalyst and a downstream oxidation catalyst. The detailed configuration of such a further-developed exhaust gas unit is dependent on the respective application and is not subject matter of the present technical teaching.

The invention is illustrated below with the aid of a few examples and figures. The figures show:

Figure 1: Measured lean running times of the total system as a function of temperature upstream of the catalyst close to the engine ("NO_x window") in the thermally aged state (■), after reactivation at 375°C in the underbody catalyst (UB) and $\lambda = 1$ (▲) and after reactivation at 650°C in the underbody catalyst (UB) and $\lambda = 1$ (○).

Figure 2: Observed HC conversions of the total system as a function of temperature upstream of the catalyst close to the engine in the thermally aged state (■), after reactivation at 375°C in the underbody catalyst (UB) and λ = 1 (▲) and after reactivation at 650°C in the underbody catalyst (UB) and λ = 1 (○).

Figure 3: Internal combustion engine with two-stream exhaust gas purification unit which, in each exhaust gas train, contains an exhaust gas purification converter close to the engine and a second exhaust gas purification converter located in the underbody region of the vehicle.

Example:

The reactivation of thermally aged nitrogen oxide storage catalysts was examined on an engine test bed using a lean-burn engine (6-cylinder engine, 3.5 l capacity, direct petrol injection). A two-stream exhaust gas purification unit was used.

The structure of this exhaust gas purification unit is shown schematically in figure 3. Each train of the two-stream exhaust gas purification unit of the engine (1) was equipped with two converter housings of which one was in a position close to the engine (2) and the other was arranged at a place equivalent to the underbody position of the vehicle (3). The reference numerals (4) and (5) each denote an exhaust gas train. Reference numeral (6) schematically denotes the offtake points for exhaust gas to be analyzed and at the same time represents the exhaust gas analyzers. The reference numerals (7) and (8) denote mufflers.

The converters in exhaust gas train (4) of the two-stream unit were equipped with mass-produced catalysts. The exhaust gas of this exhaust gas train was not examined. The catalysts used served merely to maintain realistic exhaust gas backpressure conditions.

In the exhaust gas train (5), nitrogen oxide storage catalysts as described in EP 1317953 A1 were used both in the converter (2) close to the engine and also in the equivalent converter (3) in the underbody position. These catalysts contain, in accordance with claim 10 in the abovementioned application, a storage material containing a basic barium compound as storage component applied to a high-surface-area support material based on cerium oxide. The composition of the exhaust gas to be treated in this train of the exhaust gas purification unit was analyzed by means of a suitable exhaust gas analysis facility (6) (AMA 2000; from Pierburg).

A catalyst having a catalyst volume of 0.82 l was used in the converter close to the engine (2) of the exhaust gas train (5). The cell count was 93 cells per square centimeter. In the underbody region (3), two catalysts having a total volume of 2 l were used, with each catalyst having a volume of 1 l. These catalysts had 62 cells per square centimeter.

The catalytic coating of all catalysts used in these studies corresponded to a catalyst formulation from EP 1317953 A1, which is hereby incorporated by reference with regard to the details of the formulation. The storage material of this catalyst is barium oxide on a cerium/zirconium mixed oxide (90% by weight of cerium oxide and 10% by weight of zirconium oxide).

Before installation in the converter housings, the catalysts were calcined at 950°C in a furnace for a period of 12 hours in order to bring about defined thermal ageing of the catalysts.

The thermally aged catalyst systems were then characterized in the configuration described on the engine test bed. For this purpose, the engine was operated under lean conditions at various loads, so that temperatures in the range from 200 to 470°C resulted upstream of the catalyst close to the engine. The nitrogen oxide emission was determined by means of an NO_x sensor located in the exhaust gas train (5) downstream of the underbody catalyst (3). On reaching a critical nitrogen oxide concentration threshold downstream of the underbody catalyst, the lean phase was stopped and the nitrogen oxide regeneration was commenced by switching over to rich operating conditions. The end of the regeneration phase was likewise detected by means of the NO_x sensor when this indicated breakthrough of regeneration agent. The lean running times determined in this method were plotted as a function of the temperature of the catalyst close to the engine in order to characterize the nitrogen oxide storage behavior ("NO_x window"; figure 1).

The hydrocarbon conversion of the exhaust gas system was calculated from the hydrocarbon emissions measured in the raw emission and downstream of the underbody catalyst according to the following formula:

$$\text{HC conversion [\%]} = \frac{HC_{\text{raw emission}} - HC_{\text{exhaust gas (5)}}}{HC_{\text{raw emission}}} \cdot 100$$

After the characterization of the catalyst system in the thermally aged state, reactivation was carried out by firstly switching over to a stoichiometric air/fuel ratio at the hottest

operating point selected within the "NOx window" and switching off the exhaust gas recirculation for one hour. This resulted in temperatures in the underbody catalyst of 375°C. After the end of the reactivation time, the exhaust gas recirculation was reinstated, the engine was "set back" to lean operating conditions and the characterization was repeated in accordance with the above-described routine.

Since the decomposition of barium cerate in the presence of carbon dioxide is preferably carried out at relatively high temperatures, a further reactivation experiment was carried out immediately after the characterization after reactivation at $\lambda = 1$ and with exhaust gas recirculation turned off. An engine operating point with a stoichiometric air/fuel ratio at which the underbody catalyst was heated to 650°C was chosen. After a period of operation of one hour under the conditions mentioned, the engine was switched back to lean operating conditions and the above-described characterization procedure was carried out for a third time.

The results of the characterizations are shown in figures 1 and 2.

Figure 1 shows the measured lean running times of the total system as a function of the temperature upstream of the catalyst close to the engine ("NO_x window") in the thermally aged state (■), after reactivation at 375°C in the underbody catalyst (UB) and $\lambda = 1$ (▲) and after reactivation at 650°C in the underbody catalyst (UB) and $\lambda = 1$ (○). Even the reactivation at 375°C (UB) led to a significant lengthening of the lean running time over the entire temperature range. At the operating point at 370–380°C upstream of the catalyst close to the engine, which is optimal for the catalyst system, an improvement in the lean running time from 59 seconds to 130 seconds, i.e. by 120%, was achieved.

The reactivation at 650°C (UB) was able to achieve only a small further improvement over the first reactivation at 375°C (UB). This is presumably due to an almost optimal effect having been achieved after the first reactivation.

Figure 2 shows the observed hydrocarbon conversions of the total system as a function of the temperature upstream of the catalyst close to the engine. Here, the curve denoted by (■) shows the performance of the total system in the thermally aged state. After reactivation at 375°C in the underbody catalyst (UB) and $\lambda = 1$, the conversion curve denoted by (▲) is obtained. (○) represents the hydrocarbon conversion of the total system after reactivation at 650°C in the underbody catalyst (UB) and $\lambda = 1$. Comparison of the curves shows that the reactivation results in a slight improvement in

the hydrocarbon conversion in the temperature range from 200 to 400°C. However, the data demonstrate that, in particular, the reactivation procedure according to the invention does not lead to damage to noble metal sites. The latter are of critical importance to the oxidative conversion of hydrocarbons and carbon monoxide.

The experimental data demonstrate that the mode of operation according to the invention at $\lambda = 1$ in a suitable temperature range leads to partial restoration of the activity of thermally aged nitrogen oxide storage catalysts when the nitrogen oxide storage catalysts contain a basic barium compound on a support material based on cerium oxide as nitrogen oxide storage material.

Claims

1. A method for the on-board reactivation of a thermally aged nitrogen oxide storage catalyst which comprises basic strontium or barium compounds or strontium and barium compounds on a support material containing cerium oxide and additionally contains strontium and/or barium compounds with the support material formed by thermal ageing and which is used for purification of exhaust gases of a motor vehicle having a lean-burn engine, wherein the compounds of strontium and/or barium with the support material are decomposed during normal driving operation by treatment with a gas mixture which contains carbon dioxide, optionally water vapor and optionally nitrogen oxides and is generated by the engine of the vehicle, with the oxygen content of the gas mixture during the decomposition process not exceeding the air index $\lambda = 1$.

2. The method as claimed in claim 1, wherein the nitrogen oxide storage catalyst is a constituent of an exhaust gas purification unit on a vehicle having a lean-burn engine and the generation of the gas mixture required for reactivation of the catalyst is carried out in operating states of the lean-burn engine having exhaust gas temperatures in the range from 200°C to 950°C.

3. The method as claimed in claim 2, wherein a stoichiometric air/fuel ratio is set in the operating state of the lean-burn engine used for reactivation of the catalyst so that the exhaust gas used for reactivation has an air index of $\lambda = 1$ and the duration of the reactivation is at least a few minutes.

4. The method as claimed in claim 2, wherein a substoichiometric air/fuel ratio is set in the operating state of the lean-burn engine used for reactivation of the catalyst so that the exhaust gas used for reactivation has an air index of $\lambda < 1$ and the duration of the reactivation is at least a few minutes.

5. The method as claimed in claim 3 or 4, wherein the exhaust gas used for reactivation of the catalyst contains 5–20% of carbon dioxide, 5–15% by volume of water vapor, 0–5% by volume of nitrogen dioxide and essentially nitrogen as balance.

6. The method as claimed in claim 3 or 4, wherein the exhaust gas purification unit contains at least one catalytic converter.

7. The method as claimed in claim 6, wherein the exhaust gas purification unit contains at least one catalytic converter close to the engine and an underbody converter.

8. The method as claimed in claim 7, wherein both converters contain at least one nitrogen oxide storage catalyst.

9. The method as claimed in claim 7, wherein the converter close to the engine contains a three-way catalyst and the underbody converter contains a nitrogen oxide storage catalyst.

10. The method as claimed in claim 7, wherein the converter close to the engine contains a diesel oxidation catalyst and the underbody converter contains a nitrogen oxide storage catalyst.

11. The method as claimed in claim 9 or 10, wherein the temperature upstream of the underbody converter is from 300°C to 850°C.

12. The method as claimed in claim 1, wherein a reducing agent is introduced directly into the exhaust gas train upstream of the first nitrogen oxide storage catalyst present in the exhaust gas unit in order to adjust the air index of the gas mixture generated by the engine.

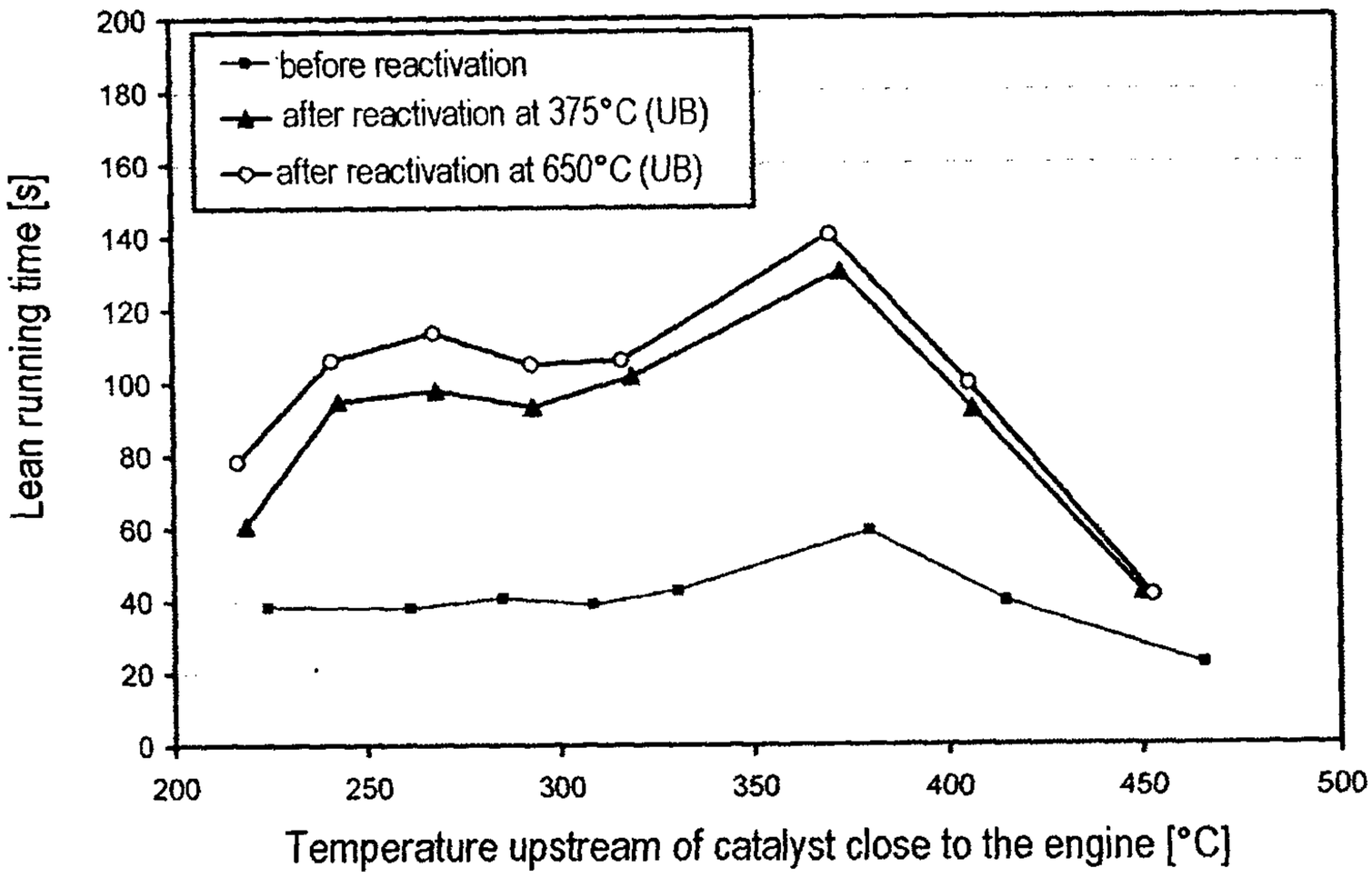


Figure 1

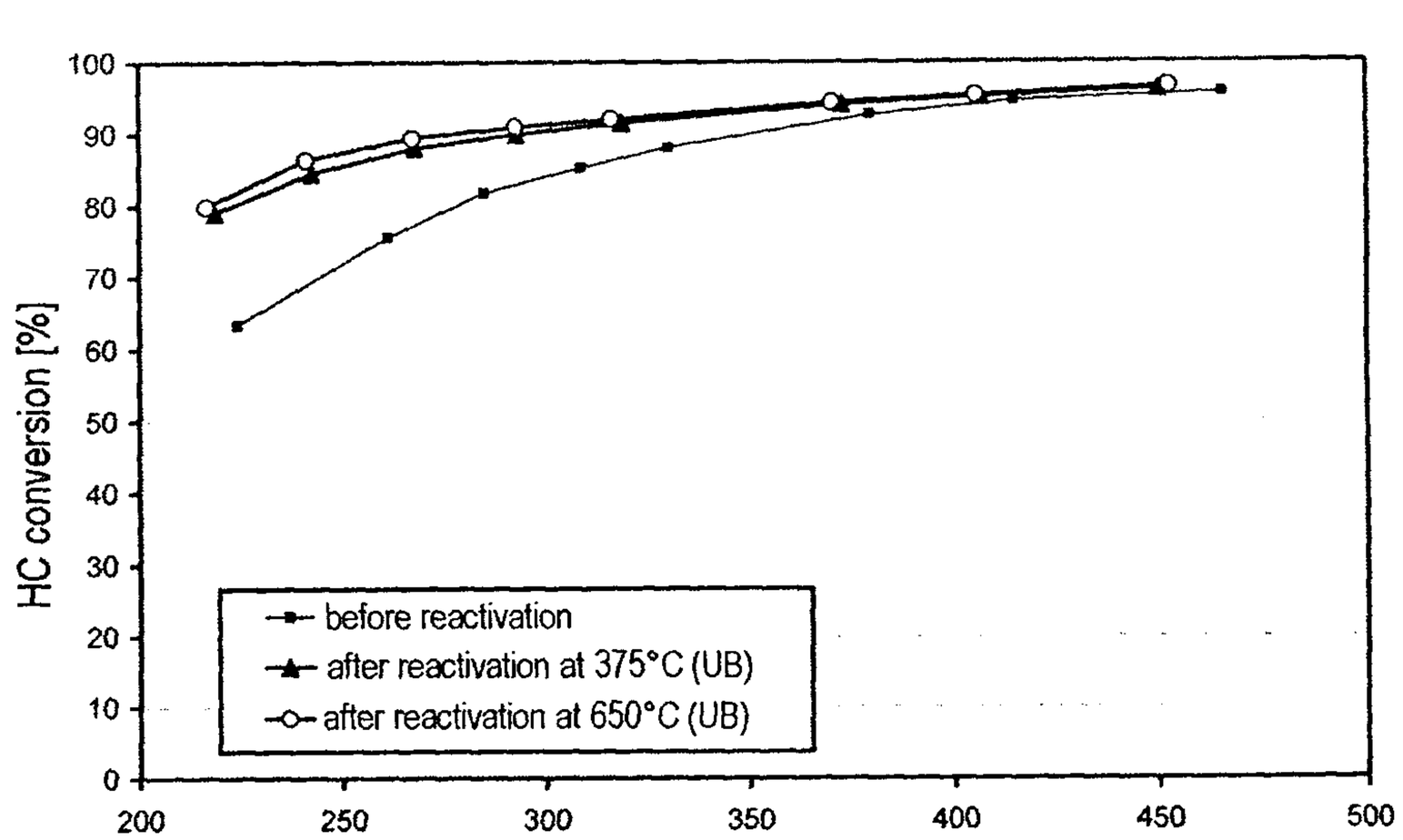


Figure 2

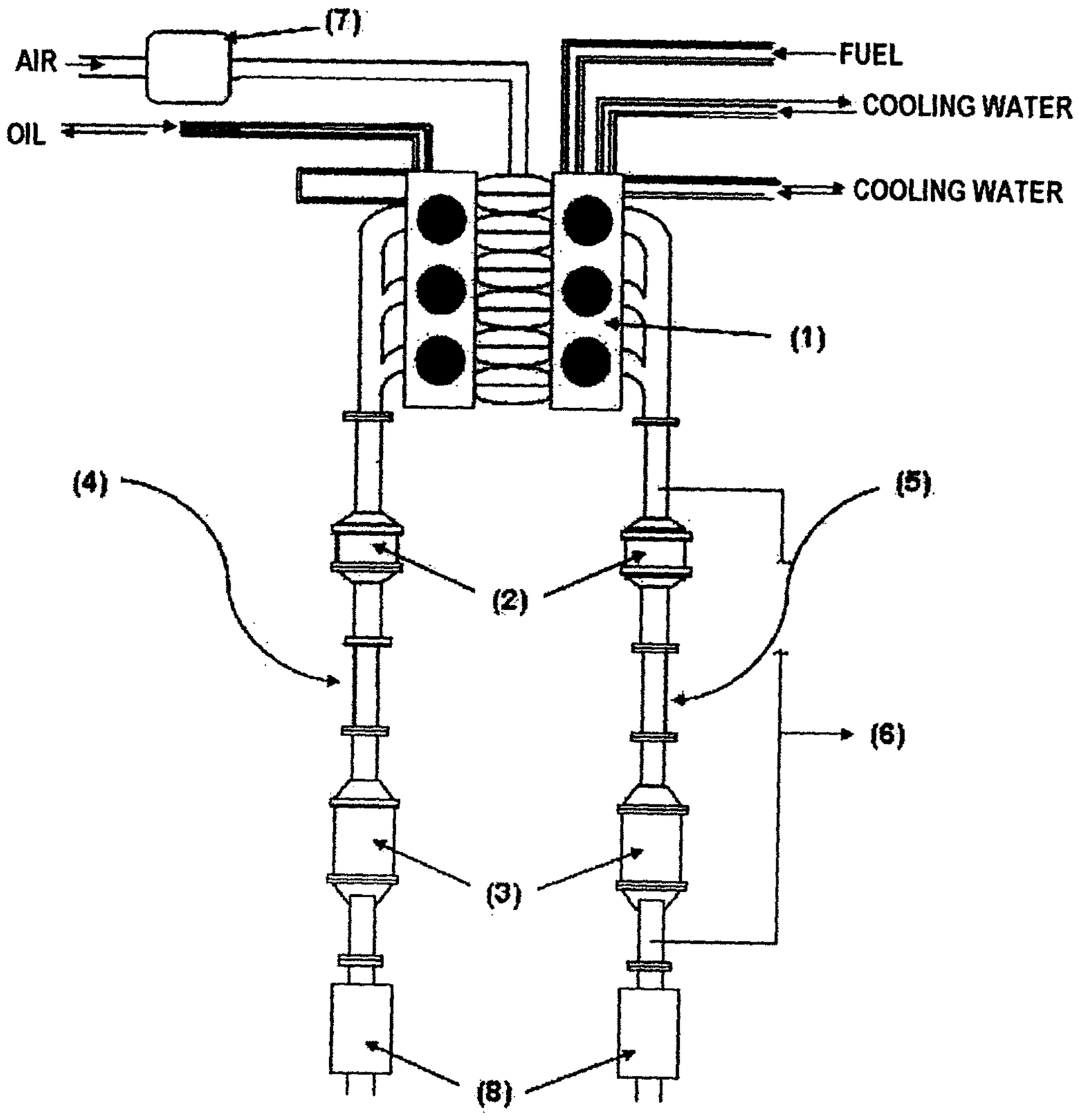
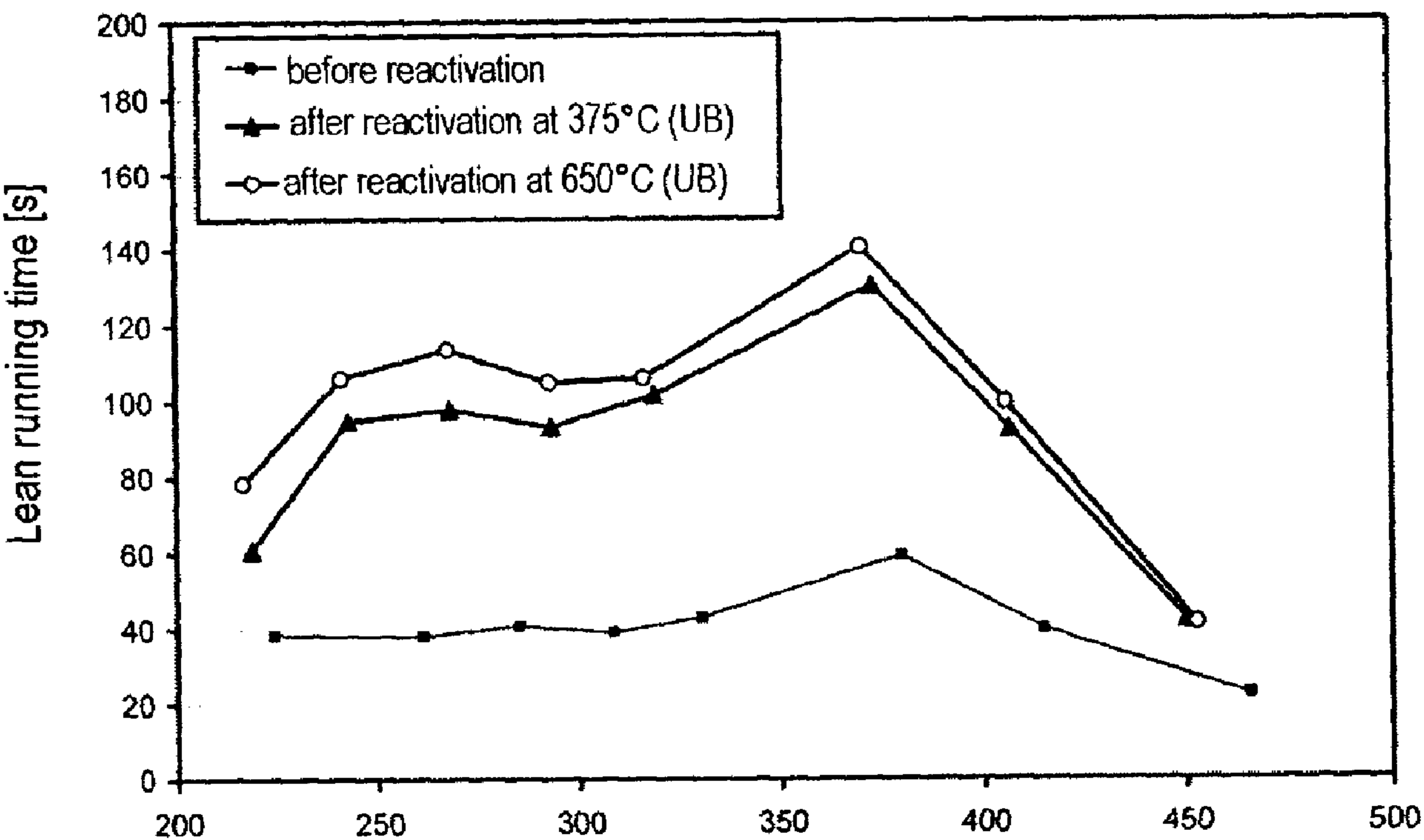


Figure 3


before reactivation
after reactivation at 375°C (UB)
after reactivation at 650°C (UB)
Lean running time [s]
200
180
160
140
120
100
80
60
40
20
0
200
250
300
350
400
450
500
Temperature upstream of catalyst close to the engine [°C]