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(57) **Abrégé/Abstract:**

Exhaust gas catalysts are poisoned by sulphur species in the fuel, but if mounted under-floor do not reach a temperature at which sulphur may be removed. Periodic oxidation of CO and/or hydrocarbons on the catalyst by the addition of supplementary air can raise the temperature of the catalyst to at least 550 °C, preferably higher, and thus maintain desired catalytic activity.

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(21) International Application Number: PCT/GB98/02483 (22) International Filing Date: 19 August 1998 (19.08.98) (30) Priority Data: 9718059.0 28 August 1997 (28.08.97) GB (71) Applicant (for all designated States except US): JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): ANDERSEN, Paul, Joseph [US/US]; 355 Brighton Road, Norristown, PA 19401 (US). BALLINGER, Todd, Howard [US/US]; 911 Jode Road, Audubon, PA 19403 (US). LAFYATIS, David, Scott [US/US]; 333 Lancaster Avenue #709, Frazer, PA 19355 (US). RAJARAM, Raj, Rao [MU/GB]; 34 Buckland Avenue, Slough SL3 7PH (GB). WALKER, Andrew, Peter [GB/GB]; 83 St. Nicholas Road, Wallingford OX10 8HY (GB). (74) Agent: WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: IMPROVEMENTS RELATING TO CATALYSTS		
(57) Abstract <p>Exhaust gas catalysts are poisoned by sulphur species in the fuel, but if mounted under-floor do not reach a temperature at which sulphur may be removed. Periodic oxidation of CO and/or hydrocarbons on the catalyst by the addition of supplementary air can raise the temperature of the catalyst to at least 550 °C, preferably higher, and thus maintain desired catalytic activity.</p>		

IMPROVEMENTS RELATING TO CATALYSTS

This invention concerns improvements relating to catalysts, more especially it concerns improvements in automobile emission catalysts.

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The use of such catalysts, also known as catalytic convertors, is very well established in the automobile industry in view of the exhaust gas emission regulations which are in force in most countries. The most common catalysts use a platinum group metal ("PGM") especially one or more of Pt, Pd and Rh, carried on an oxidic high surface area washcoat
10 which is one or more of Al_2O_3 , CeO_2 , ZrO_2 including mixed oxides thereof or the like. The support for the catalyst is generally a low pressure-drop flow-through honeycomb manufactured from an extruded ceramic, *eg* cordierite, or from a metal honeycomb.

Gasoline contains varying amounts of sulphur depending upon its origins and the
15 amount and type of refining it has been subjected to. Sulphur is a well-known poison of catalyst activity in such catalysts. We believe that the deactivating effect of sulphur may be due to adsorption on either the precious metal or on the support. We have found that sulphur may be removed by increasing the temperature of the catalyst, but that under lean operating conditions, that is when the overall composition of the exhaust gases leaving the engine is
20 oxidising, the temperature required for sulphur removal is higher than under rich conditions. Indeed, we have found that for certain catalysts, the minimum temperature for sulphur removal is 625°C under lean conditions. This temperature is higher than the catalyst would normally be exposed to in its usual under-floor position mounted on the automobile.

25 EP 580389 (Toyota) discloses the removal of SO_x from a NO_x absorbent-type catalyst which is used to treat the exhaust gases from a lean-burn gasoline internal combustion engine, by decreasing the oxygen concentration in the exhaust gases, thus making them rich. That is, SO_x is being removed from the NO_x absorbent by chemical means. JP 4161251 (Mitsubishi) teaches the removal of SO_x from a catalyst for a lean burn
30 internal combustion engine such as a diesel engine, by heating the catalyst to $450\text{-}800^\circ\text{C}$. It is plain from the drawings that significant heating is required (600°C for 1 hour) in order

to approximate the S-free conversion. Heating at 500°C did not give such good results. Most diesel fuels have a much higher S content than gasolines. Mitsubishi also discloses in DE 19522165 a system for removing poisons from a NO_x storage catalyst by causing heating to 650°C. No experimental evidence, nor any detail of regeneration times, are disclosed.

5

The present invention provides a system comprising a gasoline-fuelled internal combustion engine, a three-way catalyst mounted under-floor and arranged to continuously have exhaust gas passed therethrough, and an engine management system, said system being so designed and constructed that during at least one portion of every operation of the engine, the engine management system initiates an operating condition which raises the catalyst temperature to at least 550°C, preferably at least 600°C, more preferably at least 625°C, whereby sulphur poisoning of the catalyst is reduced.

10

The invention also provides a method of reducing sulphur poisoning of a three-way catalyst, which method comprises intermittently raising the temperature of the catalyst to at least 550°C, preferably at least 600°C, more preferably at least 625°C whilst continuously passing exhaust gas therethrough, providing said intermittent heating takes place at least once every engine operation.

15

The internal combustion engine and its associated controls may be desirably designed in a first embodiment to operate essentially under stoichiometric conditions.

20

A preferred catalyst for use in this first embodiment incorporates palladium and ceria. A more preferred catalyst is one having ambient temperature CO oxidation activity, as described in our prior patent applications WO 96/39576 and EP 0747581.

25

The system of the first embodiment preferably operates by intermittently oxidising CO and/or hydrocarbon by the addition of a secondary air supply just upstream of the catalyst. The engine management system is therefore designed to initiate a condition in which the exhaust gas is enriched with CO and/or hydrocarbon, and secondary air is added. Accordingly, the exotherm from such oxidation raises the catalyst temperature.

30

The first embodiment of the present invention may be operated in several different ways. In a first method, especially when using the preferred catalysts, the engine management system provides a very rich cold start. Oxidation of CO and unburnt hydrocarbon species (using a secondary air supply) on the catalyst immediately begins to
5 raise the catalyst temperature to a temperature at which sulphur removal under lean conditions takes place, that is preferably above 625°C. More preferably, the rich cold start is continued to bring the catalyst to a temperature of 800-850°C or higher, in order to remove virtually all sulphur species from the catalyst.

10 A second method, which may be combined with the first, utilises a periodic enrichment to, for example, an air/fuel ratio of 10-14 for a pre-set time, for example 5-100 seconds, during normal running, combined with secondary air addition. The catalyst will already be at a normal operating temperature of at least 400°C and therefore does not require as much chemical energy to raise its temperature to an effective sulphur-removal
15 temperature as does the first embodiment which begins at ambient temperature. In such a second method, the period between initiations of the high temperature may be pre-set in the engine management system memory, or may be variable according to operating conditions and/or either the sulphur content of the fuel, eg as sensed, or some form of feed-back of sulphidation of the catalyst.

20 A modification of this second method arises in a preferred design in which the said catalyst is supplemented by another catalyst, preferably in a close-coupled position close to the engine. The close-coupled catalyst is mounted upstream of the secondary air inlet. This offers particular benefits in that during the high temperature phase, NOx reduction on the
25 main catalyst is less effective (because of the lean condition due to secondary air addition), but the close-coupled catalyst, which is exposed to the enriched engine-out condition, can still provide NOx removal.

A third method involves removal of sulphur under rich conditions, which may be
30 achieved at a lower catalyst temperature than when the exhaust gas is stoichiometric or lean. The normal operating temperature of the catalyst is still generally below that at which

sulphur may be removed. It is therefore again necessary to raise the catalyst temperature which may be done by enrichment, either on start-up or periodically during operation, by adjusting the air-fuel ratio fed to the engine or by supplementary fuel addition into the exhaust gas stream. Supplementary air addition provides the conditions for exothermic oxidation on the catalyst raising its temperature to or above the required level. Once the required temperature has been reached, suitably at least 550°C, preferably at least 650°C, the supplementary air may be terminated or reduced, so that the exhaust gases are rich, that is there is an excess of reducing species.

10 A second embodiment of the present invention utilises instead of, or to supplement, oxidative heating as in the first embodiment, electric resistive heating of the catalyst. This may be effected by directly heating the catalyst or by positioning an electric heating element upstream of the catalyst. Electrically heated catalysts have been proposed to speed light-off of catalysts upon start-up from cold but because of the high power requirements, have not met with general acceptance. In this embodiment, because it is envisaged that electric heating will be initiated during operation of the engine, when the catalyst is already at its operating temperature, the power required to reach the desired temperature according to the present invention is comparatively low, and since the time for reaching the desired temperature is not so important, the total power required in this embodiment need not exceed the power that can be provided by the vehicle's on-board generation capacity, eg the engine's alternator. An electrically heated catalyst as proposed in the art requires a second battery, with consequential design, engineering and weight costs. We are not aware of any prior proposal which contemplates electric heating of a catalyst in a gasoline-powered vehicle at any point during normal operation of the engine.

25

This second embodiment of the invention is believed to have particular application for lean-burn gasoline engines, especially for gasoline direct injection. For such lean-burn engines, the catalyst desirably comprises a NO_x-storage component such as baria and/or calcia.

30

It will be appreciated that the actual conditions, time periods and other parameters relevant to sulphur removal depend upon the engine and emission system design and general operating conditions, as well as the results desired, and may be determined by conventional optimisation.

5

The first embodiment of the invention is believed to offer particular advantages with the preferred catalysts mentioned above, and permits the maintenance of low temperature light-off capability.

10

The invention will now be described by way of example only.

1. Preparation of Pd/CeO₂ Catalyst

15

Commercially available CeO₂ particles were impregnated using tetraammine palladium hydrogen carbonate solution so that the PGM content was 8%Pd by weight. This was then coated onto a 400 cells *per* square inch (62 cells/cm²) monolith at a loading of 3g/in³ (0.18g/cm³).

2. Experimental Evaluation Protocols

20

In order to test catalysts on a micro reactor, the following evaluation procedures were adopted.

Test 1 Protocol

25

Prior to experiment, the catalyst is heated to 425°C in a stream of argon with 5%O₂. The catalyst is then cooled to ambient temperature in this stream. Temperature ramp at the catalyst inlet starts at time=0 from ambient temperature, as shown in Figure 1. At time=0, the following species are also fed to the reactor (GHSV=30,000);

30

500ppm NO
600ppm C₃H₆
15% CO₂
10% H₂O
5 4% CO

Evaluation is performed by measuring the average CO conversion during the first 20 seconds of the experiment (while the catalyst inlet temperature is still below 50°C).

10 Test 2 Protocol

Prior to experiment, the catalyst is heated to 425°C in a stream of argon with 5%O₂. The catalyst is then cooled to ambient temperature in this stream. Temperature ramp at the catalyst inlet starts at time=0 from ambient temperatures, as shown in Figure 1. At time=0,
15 the following species are also fed to the reactor (GHSV=30,000)

15% CO₂
4% CO

Evaluation is performed by measuring the average CO conversion during the first 20
20 seconds of the experiment (while the catalyst inlet temperature is still below 50°C).

This test protocol is somewhat less stringent than the Test 1 protocol, because there are fewer inhibiting species present in the feed.

25 For a series of further tests, catalysts were aged by exposure to a variety of gases and conditions. The gas concentrations for tests 1A to 1E are specified in the Table below, the balance being N₂, under the conditions specified below for the various tests.

Test	C ₃ H ₆	NO _x	SO ₂	O ₂	CO ₂	CO
1A	600ppm	500ppm	0ppm	4%	15%	1.5%
1B	600ppm	500ppm	5ppm	4%	15%	1.5%
1C	600ppm	500ppm	5ppm	11%	15%	8.5%
1D	600ppm	500ppm	5ppm	11%	15%	9%/1.5% cycles
1E	600ppm	500ppm	5ppm	11%	15%	9%/1.5% cycles

3. Examples 1A, 1B and 1C: Steady-State Ageing Condition

Three identical catalyst samples were aged in a micro-reactor under lean conditions in feeds containing CO, O₂, CO₂, C₃H₆, NO at a GHSV of 100,000 and at a catalyst inlet temperature of 350°C for 14 hours. In Example 1A, the feed contained 1.5%CO and 4%O₂, and the temperature measured in the catalyst bed was 435°C.

In Example 1B, the feed contained 1.5%CO, 4%O₂ and 5ppm SO₂, and the temperature measured in the catalyst bed was 435°C.

In Example 1C, the feed contained 8.5%CO, 11%O₂ and 5ppm SO₂, and the temperature measured in the catalyst bed was 860°C.

Table 1 shows the resulting catalyst performance following these steady-state ageing conditions.

TABLE 1

Sample (ageing conditions)	%CO Conversion Protocol 1	%CO Conversion Protocol 2
1A (low temperature, no SO ₂)	97%	not tested
1B (low temperature, with SO ₂)	not tested	0%
1C (high temperature, with SO ₂)	86%	not tested

As can be seen from these results, low temperature ageing in the absence of SO₂ (Sample 1A) leaves a catalyst with excellent levels of low temperature CO oxidation activity in the stringent test protocol 1. However, the addition of sulphur to the feed during this low temperature ageing (sample 1B) completely removes all of this low temperature activity. This is caused by sulphur poisoning of the active sites. The deleterious effect of sulphur on the catalyst activity is negated, however, when the ageing is performed at elevated temperature (as in sample 1C). This is because the sulphur does not adsorb onto the catalyst under these conditions.

4. Examples 1D and 1E - Cycled Ageing Condition

The above Example shows that by keeping the catalyst continually hot (>800°C) under normal lean operation the catalyst can maintain its excellent low temperature activity. However, under real driving conditions it may be more practical (*ie* fuel efficient) to expose the catalyst to high temperature conditions only on a periodic basis.

Two more catalysts were aged in the micro reactor under lean conditions in feeds containing CO, O₂, CO₂, C₃H₆, NO and 5ppm SO₂ at a GHSV of 100,000 and at a catalyst inlet temperature of 350°C for 14 hours. In both ageings, the oxygen concentration was held at 11%.

In Example D: the catalyst was aged under cyclic conditions with a 300-second period;

100 seconds: 9% CO, bed temperature $\approx 880^{\circ}\text{C}$;

200 seconds: 1.5%CO, bed temperature $\approx 420^{\circ}\text{C}$;

5

In Example 1E: the catalyst was aged under cyclic conditions with a 1000-second period;

100 seconds: 9%CO, bed temperature $\approx 800^{\circ}\text{C}$;

900 seconds: 1.5%CO, bed temperature $\approx 430^{\circ}\text{C}$.

10

Table 2 shows the evaluation results following these cycled ageing conditions.

TABLE 2

15

Sample	%CO Conversion Protocol 1	%CO Conversion Protocol 2
1D	71%	91%
1E	38%	62%

20

Table 2 shows that high levels of low temperature CO activity are retained by the catalysts following such a cycled ageing protocol. It is also worth noting that using mass spectrometry, SO_2 was identified leaving the catalyst during the high temperature portions of these cycles. Thus, such a cycled ageing protocol may be used to deliberately remove sulphur and enhance the activity of such catalysts.

25

CLAIMS:

1. A system comprising:
 - a gasoline-fuelled internal combustion engine, wherein the engine operates at substantially stoichiometric conditions during normal operation;
 - a three-way catalyst (TWC) mounted under-floor and arranged in an exhaust passage to have exhaust gases passed continuously therethrough; and
 - an engine management system, wherein the engine management system is programmed to initiate a condition of the system in which the engine exhaust gases are enriched with at least one of CO and hydrocarbons during cold start when the engine is operated under rich conditions and under any driving conditions, and secondary air is added to the engine exhaust gases in the exhaust passage upstream of the underfloor TWC to provide lean conditions over the underfloor TWC and to cause an exotherm by oxidation of the at least one of CO and hydrocarbons over the underfloor TWC thereby to raise the temperature of the underfloor TWC to at least 550 °C, whereby sulphur poisoning of the underfloor TWC is reduced, during at least one portion of every operation of the engine.
2. A system according to claim 1, wherein the underfloor TWC comprises palladium and ceria.
3. A system according to claim 1 or 2, further comprising an additional TWC close-coupled to the engine and upstream of a point of secondary air addition.
4. A system according to claim 1, wherein sufficient secondary air is added to provide lean conditions over the underfloor TWC.
5. A method of reducing sulphur poisoning of a three-way catalyst (TWC) in an exhaust system of a gasoline-fuelled internal combustion engine, comprising the steps of:
 - operating the engine at substantially stoichiometric conditions during normal operation;

intermittently enriching the exhaust gases exiting the engine with at least one of CO and hydrocarbons during cold start when the engine is operated under rich conditions and under any driving conditions; and

adding secondary air to the exhaust gases upstream of the TWC to provide lean conditions over the TWC thereby to cause catalytic oxidation of the at least one of CO and hydrocarbons to cause heating of the TWC, thereby to raise the temperature of the TWC to at least 550 °C, whilst continuously passing exhaust gases therethrough, provided that the intermittent enrichment and air addition takes place at least once every engine operation.

6. A method according to claim 5, wherein heating is carried out to raise the catalyst temperature to at least 600 °C.

7. A method according to claim 5, wherein the step of intermittently enriching the exhaust gases is done for a pre-set time between 5–100 seconds.

8. A method according to claim 5, wherein sufficient secondary air is added to provide lean conditions over the TWC.

Fig. 1.

