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(54) Title: SYSTEM FOR THE REMOVAL OF PARTICULATE MATTER AND NOXIOUS COMPOUNDS FROM ENGINE EXHAUST GAS

(57) Abstract: System for the removal of noxious compounds and particulate matter from exhaust gas of a compression ignition engine comprising a three way catalyst unit having an NH_3-SCR activity, an ammonia oxidation activity and an adsorption activity of volatile vanadium and tungsten compounds volatilized off an upstream SCR active catalyst.

System for the removal of particulate matter and noxious compounds from engine exhaust gas

The present invention relates to a system for the removal of volatile organic compounds, particulate matter and nitrogen oxides (NOx) from exhaust gas of a compression ignition engine.

The exhaust system of modern vehicles with lean burning engines is typically equipped with an oxidation catalyst, a particulate filter and a catalyst for the selective reduction of NOx (SCR) in presence of a reduction agent.

Oxidation catalysts being active in the oxidation of volatile organic compounds and carbon monoxide and SCR catalysts are known in the art and disclosed in numerous publications.

Typically employed particulate filters (DPF) in diesel exhaust gas cleaning systems, are wall flow filters with a plurality if inlet and outlet channels. The inlet channels are closed at their outlet side and the outlet channels are closed at their inlet side, so that the gas flowing into the filter is forced through porous walls defining the channels, whereby particulate matter is filtered off the gas.

To meet future emission regulations for diesel passenger cars and trucks requires usage of both diesel particulate filter (DPF) technology and NOx reduction catalyst. Due to its potential for fuel optimization and high efficiency in NOx removal, selective catalytic reduction using ammonia as a reductant (NH3-SCR) is presently the preferred technology for NOx reduction.

The SCR catalyst can be arranged as a separate unit upstream and/or downstream the DPF. It has also been suggested in the art providing the DPF with an SCR catalyst to obtain more compact cleaning systems.

Catalysts for use in ammonia SCR are well known in the art. Of those, catalysts based on V_2O_5 and WO_3 supported on a TiO_2 carrier provide a fundamental solution to effectively reduce NOx emissions from Diesel fueled vehicles by means of the Selective Catalytic Reduction (SCR) with ammonia. Compared to alternative strategies for NOx emission control like exhaust gas recirculation (EGR) and zeolite-based catalysts, a great advantage of vanadium-based SCR catalysts is their SCR efficiency, robustness to sulfur and their price.

When operating a cleaning system with a DPF, particulate matter trapped in the filter must be form time to time or continuously be removed in order to avoid pressure drop over the filter. An increased pressure drop costs fuel penalty. Therefore, particulate matter accumulated on the filter walls at inlet side of the filter must be removed either by active regeneration, wherein particulate matter is catalytically burned off in contact with an oxidation catalyst supported on the filter walls in combination with oxygen in exhaust gas at increased exhaust gas temperatures or by non-catalytic passive regeneration.

In the passive soot regeneration the DPF is regenerated at temperatures below 550°C with NO_2 that is generated over the upstream DOC by oxidation of NO. Regeneration with oxygen in the exhaust gas should be avoided in order to control the temperature below 550°C. If the filter uncontrolled regenerates with oxygen the temperature could rise above 550°C.

Despite being effective SCR catalysts, vanadium oxide based catalysts contain V_2O_5 as an essential component, which is toxic. Reports in the literature suggest that bulk V_2O_5 has a significant vapor pressure at temperatures relevant to the catalyst operation, and both V and W compounds react with water to form species with increased vapor pressure.

Measurable amounts of vanadium are first released at temperatures of above 600°C, which is around the highest applicable working temperature of these systems.

Consequently, there is a risk of V and W volatile compounds can vaporize from the $V_2O_5/WO_3/TiO_2$ SCR catalysts in particular when integrated in the DPF. The temperature in V-SCR catalysed DPF has the highest probability of being exposed to temperatures exceeding 600°C, but in severe events the temperature in the V-SCR catalyst can also increase above 600°C and trigger evaporation of these compounds.

Beside the risk of emission of vanadium and tungsten compounds into the atmosphere, ammonia slip from the SCR reaction has also to be considered. To obtain a maximum NOx conversion, ammonia is typically added to the exhaust gas in over stoichiometric amounts and unreacted ammonia is emitted to the atmosphere.

The present invention seeks to solve the above problems caused by employing vanadium and tungsten oxides as effective ammonia SCR catalyst and over stoichiometric amounts of ammonia reductant in the SCR reaction in a system for the removal of particulate matter and noxious compounds including nitrogen oxides from an engine exhaust gas by combining a vanadium and tungsten adsorbent with an ammonia oxidation catalyst.

Thus, the present invention is in its broadest aspect a system for the removal of volatile organic compounds, particulate matter and nitrogen oxides from exhaust gas of a compression ignition engine comprising
(a) an oxidation unit with a catalyst active in oxidation of volatile organic compounds and carbon monoxide to carbon dioxide and water and nitrogen oxide to nitrogen dioxide;
(b) means for introducing a urea solution into the exhaust gas from unit (a);
(c) a downstream catalysed wall flow particulate filter consisting of a plurality of longitudinal inlet flow channels and outlet flow channels separated by gas permeable porous partition walls, each inlet flow channel having an open inlet end and a closed outlet end, and each outlet flow channel having a closed inlet end and an open outlet end, the wall flow filter is catalysed with an NH_3-SCR active catalyst comprising oxides of vanadium and tungsten arranged within the gas permeable porous partition walls and/or on the plurality of the inlet and/or outlet channels of the wall flow particulate filter;

(d) a downstream three way catalyst unit having an NH_3-SCR activity, an ammonia oxidation activity and an adsorption capacity for volatile vanadium and tungsten compounds volatilized off the SCR active catalyst of the particulate filter (c), the three way catalyst comprising high surface compounds selected from high surface metal oxides, zeolites, silica, non-zeolite silica alumina, and mixtures thereof.

Several oxides have the property to adsorb evaporated compounds of vanadium and tungsten. Oxides of vanadium, tungsten and titanium admixed with at least one of a high surface ceria, alumina, silica, zirconia, non-zeolite silica alumina and zeolites, have shown as useful V and W compounds adsorbent and are at the same time active in the SCR reaction. These adsorbents are preferably combined with an ammonia slip catalyst (ASC).

Typical ASC formulations consist of an ammonia oxidation function based on platinum, optionally combined with palladium on an alumina or titania carrier and an SCR active catalyst. In preferred formulations for use in the invention the V,W adsorbent is applied together with an SCR catalyst as a top layer on a bottom layer with the ammonia oxidation catalyst. Both layers can contain binding phases of oxide ceramics as alumina, titania, silica-alumina that have V,W adsorbing capacity.

In a specific embodiment of the invention, the three way catalyst comprises a bottom layer comprising platinum, alumina and/or titania and optionally palladium, coated on a substrate or partly or entirely forming the substrate, a top layer comprising oxides of vanadium, tungsten and titanium admixed with at least one of a high surface ceria, alumina, silica, zirconia, non-zeolite silica alumina and zeolite.

As the three way catalyst is arranged at the coldest position in the exhaust system any potentially evaporated V and W compounds will be trapped on the three way catalyst during the life time of the exhaust system on a vehicle.

High vanadium and tungsten adsorption efficiencies are achieved with a relatively thick top layer in the three way catalyst.

Thus, in preferred embodiments the top layer has layer thickness of between 40 µm and 250 µm.

In further a preferred embodiment the bottom layer has a layer thickness of between 5µm and 80µm. When the bottom layer itself forms partly or entirely the substrate the layer thickness is up to 450µm.

In order to assure sufficient permeation of ammonia from the top layer to the bottom layer, the top layer must be relatively porous.

Thus, in further a preferred embodiment the top layer has a porosity of between 20% and 80%.

Preferably the three way catalyst is arranged on a substrate with a flow through monolith shape.

When coated on a substrate in form of a flow through monolith, the amount of the top layer in the three way catalyst is between 50 and 500 g per liter of the flow through monolith.

The amount of the bottom layer in the three way catalyst is preferably between 5 and 255 g per liter of the flow through monolith, the amount depends on whether the bottom layer is coated on the surface of the monolith substrate or partly or entirely forms the monolith substrate.

High ammonia oxidation activities of the three way catalyst are obtained, when the bottom layer of the three way catalyst contains 0.0018g-0.35 g platinum and/or palladium per liter of the flow through monolith.

The top layer of the three way catalyst comprises preferably per liter of the flow through monolith 1.0g-20g vanadium pentoxide, 3g-40 g tungsten oxide, 40g-460g titania, and 0g-86g silica, 0g- 86g ceria, 0g-86g alumina, 0g-86g non-zeolite silica alumina and 0g-86g of a zeolite.

Hereby it is ensured that volatile vanadium and tungsten compounds are essentially adsorbed on the surface of titania and silica and that remaining amounts of NOx from the upstream units are selectively reduced to nitrogen and water by the SCR reaction.

In the above embodiments of the invention it is preferred that the oxidation catalyst in unit (a) upstream of the DPF comprises platinum and palladium supported on silica-alumina and/or alumina and/or titania with a weight ratio of platinum to palladium of 1:0 to 1:1.

The content of platinum and/or palladium in the oxidation catalyst is preferably 0.1g and 2g per liter catalyst.

In still an embodiment, it may be preferred that the system comprises a further SCR catalyst unit for decreasing remaining amounts of NOx in the exhaust gas from filter(c) by reaction with ammonia in contact with an SCR active catalyst comprising oxides of vanadium, tungsten and titanium, the catalyst arranged between filter (c) and three way catalyst (d).

Figure 1 displays the NOx conversion, together with the outlet concentrations of NOx, N_2O, and N_2. The performance under these conditions in NH_3-SCR is documented by a conversion of about 50-60% in the temperature range of interest (250-400 °C) with a low yield of N_2O and a high yield of N_2. Fig. 1 shows NOx conversion for NH3-SCR and outlet concentrations of NOx, N2, and N2O for a Pt/V-W-oxide based monolith three way catalyst, using a feed of 250 ppm NOx, 300 ppm NH3, 12% O2, and 4 % water in nitrogen at a space velocity of 100000 h^{-1}.

Figure 2 shows the conversion of ammonia, and selectivities to N2, NOx, N2O in the selective oxidation to ammonia. In the temperature range of interest (250-400 □C), the ammonia is almost completely converted and the reaction product consists mainly of nitrogen. Fig. 2 shows NH_3 conversion for selective oxidation of ammonia and selectivities to NOx, N_2, and N_2O for a Pt/V-W-oxide based monolith three way catalyst, using a feed of 200 ppm NH_3, 12% O_2, and 4 % water in nitrogen at a space velocity of 100000 h^{-1}.

EXAMPLE 1

This example demonstrates the performance in NH_3-SCR of a three way catalyst. The catalyst consists of Pt impregnated on a glass fiber paper based monolith that is reinforced with TiO_2, on top of which a washcoat layer, containing vanadium and tungsten, titanium dioxide and silica, having NH_3-SCR activity, is applied. The Pt content in the catalyst was 88 mg/l. The content of the SCR active washcoat layer was 197 g/l, of which 5% was silica. The catalyst was degreened at 550 °C for 1 hour prior to the performance test. The reactor feed gas consisted of 250 ppm NOx, of which less than 5% is present as NO_2, 300 ppm NH_3, 12 % O_2, and 4 % water in nitrogen. The flow rate was adjusted to reach a space velocity of 100000 h^{-1}, based on the monolith volume.

EXAMPLE 2

This example shows the performance of the three way catalyst, as characterized in Example 1, for selective oxidation of ammonia to reduce ammonia slip. The catalyst was degreened for 1 h at 550 □C. The feed gas used in this measurement was 200 ppm NH3, 12 % O2 and 4 % water in nitrogen. The flow was adjusted to reach a space velocity of 100000 h-1 based on the monolith volume.

Claims

1. A system for the removal of volatile organic compounds, particulate matter and nitrogen oxides from exhaust gas of a compression ignition engine comprising
(a) an oxidation unit with a catalyst active in oxidation of volatile organic compounds and carbon monoxide to carbon dioxide and water and nitrogen oxide to nitrogen dioxide;
(b) means for introducing a urea solution into the exhaust gas from unit (a);
(c) a downstream catalysed wall flow particulate filter consisting of a plurality of longitudinal inlet flow channels and outlet flow channels separated by gas permeable porous partition walls, each inlet flow channel having an open inlet end and a closed outlet end, and each outlet flow channel having a closed inlet end and an open outlet end, the wall flow filter is catalysed with an NH_3-SCR active catalyst comprising oxides of vanadium and tungsten arranged within the gas permeable porous partition walls and/or on the plurality of the inlet and/or outlet channels of the wall flow particulate filter;
(d) a downstream three way catalyst unit having an NH_3-SCR activity, an ammonia oxidation activity and an adsorption capacity for volatile vanadium and tungsten compounds volatilized off the SCR active catalyst of the particulate filter (c), the three way catalyst comprising high surface compounds selected from high surface metal oxides, zeolites, silica, non-zeolite silica alumina, and mixtures thereof.

2. The system of claim 1 further comprising an SCR active catalyst comprising oxides of vanadium, tungsten and titanium, the catalyst is arranged between the particulate filter (c) and the three way catalyst unit (d).

3. The system according to claim 1 or 2, wherein the three way catalyst comprises a bottom layer comprising platinum, alumina and/or titania and optionally palladium coated on a substrate and a top layer comprising oxides of vanadium, tungsten and titanium admixed with at least one of a high surface ceria, alumina, silica, zirconia, non-zeolite silica alumina and zeolite.

4. The system according to claim 3, wherein the top layer has layer thickness of between 40µm and 250µm.

5. The system of claim 3 or 4, wherein the bottom layer has a layer thickness of between 5µm and 450µm.

6. The system of any one of claims 3 to 5, wherein the top layer has a porosity of between 20% and 80%.

7. The system according to any one of claims 1 to 6, wherein the three way catalyst is coated on a substrate with a flow through monolith shape.

8. The system according to any one of claims 1 to 7, wherein the SCR active catalyst in filter (c) further comprises titania.

9. The system according to claim 7 or 8, wherein the amount of the top layer in the three way catalyst is between 50 to 500 g per liter of the substrate.

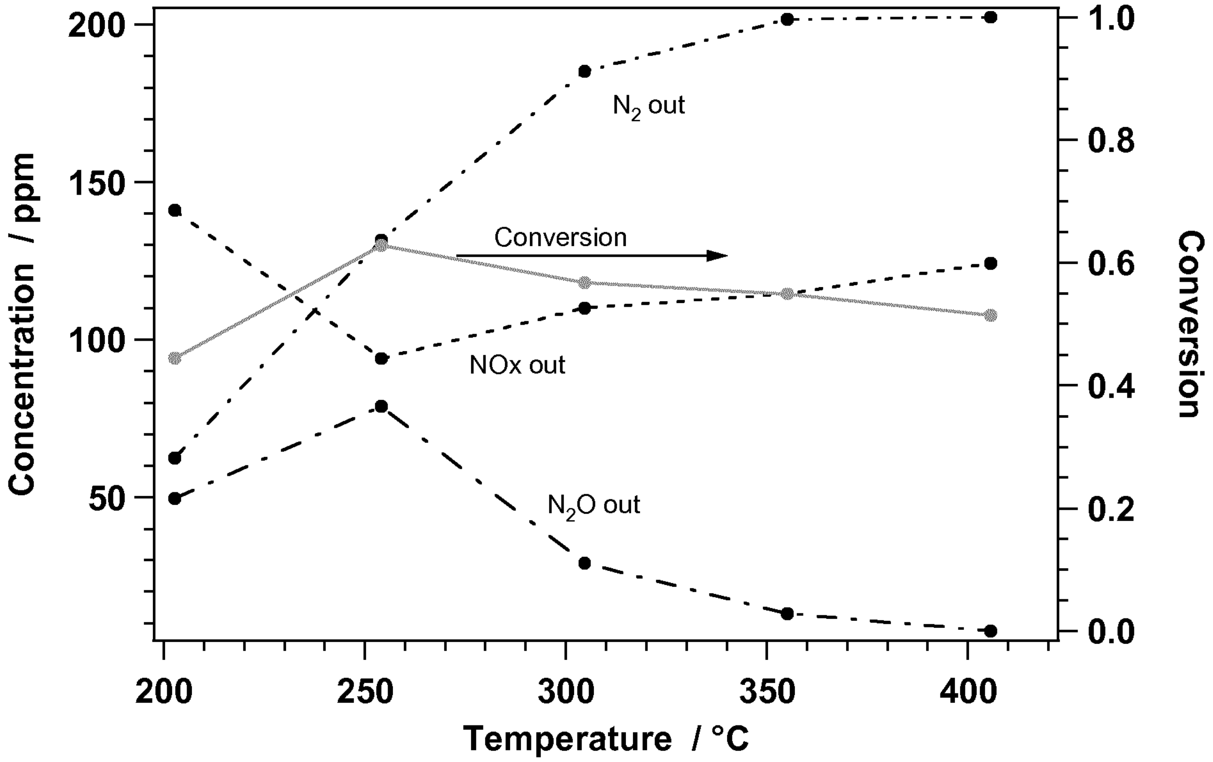
10. The system according to any one of claims 7 to 9, wherein the amount of the bottom layer in the three way catalyst is between 5 and 255 g per liter of substrate.

11. The system according to any one of claims 3 to 10, wherein the bottom layer of the three way catalyst contains 0.0018g–0.35g platinum and/or palladium per liter of the substrate.

12. The system according to any one of claims 3 to 11, wherein top layer of the three way catalyst comprises per liter of the flow through monolith 1.0g–20g vanadium pentoxide, 3g-40 g tungsten oxide, 40g–460 g titania, and 0g-86 g silica, 0g–86g ceria, 0g–86g alumina, 0g–86g non-zeolite silica alumina and 0g-86g of a zeolite.

13. The system according to any one of claims 1 to 12, wherein the oxidation catalyst in oxidation unit (a) comprises platinum and/or palladium supported on silica-alumina and/or alumina and/or titania with a weight ratio of platinum to palladium of 1:0 to 1:1.

14. The system according to claim 13, wherein the content of platinum and/or palladium is between 0.1g and 2g per liter catalyst.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Conversion
NOx out
N2O out
Concentration / ppm
Conversion
Temperature / °C
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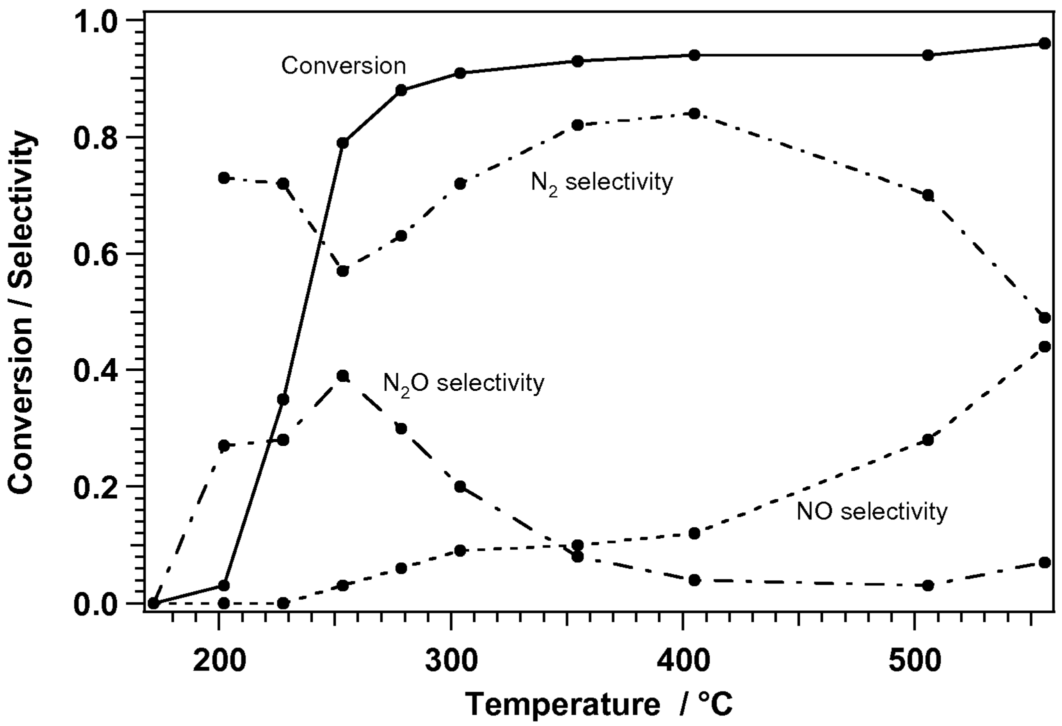
150
100
50
1.0
0.8
0.6
0.4
0.2
0.0
200
250
300
350
400

Fig. 1


Conversion
N2 selectivity
N2O selectivity
NO selectivity
Conversion / Selectivity
Temperature / °C
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0.8
0.6
0.4
0.2
0.0
200
300
400
500

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. F01N3/10 F01N3/20 F01N3/035 F01N13/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
F01N

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/166833 A1 (JOHNSON MATTHEY PLC [GB]; SPREITZER GLEN [US]; CHATTERJEE SOUGATO [US]) 6 December 2012 (2012-12-06) page 8; figure 3 -----	1-14
A	US 2010/077739 A1 (RODMAN ANTHONY C [GB] ET AL) 1 April 2010 (2010-04-01) paragraphs [0004], [0012], [0019], [0022]; figure 1 -----	1-14
A	EP 2 535 102 A1 (N E CHEMCAT CORP [JP]) 19 December 2012 (2012-12-19) paragraphs [0022], [0052]; figure 36 -----	1-14
A	EP 2 520 354 A1 (N E CHEMCAT CORP [JP]) 7 November 2012 (2012-11-07) paragraph [0019]; figure 2 -----	1-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 2012166833	A1	06-12-2012	CN 103702745	A	02-04-2014
			EP 2590730	A1	15-05-2013
			JP 5745171	B2	08-07-2015
			JP 2014522306	A	04-09-2014
			JP 2015186802	A	29-10-2015
			KR 20140010184	A	23-01-2014
			KR 20150027839	A	12-03-2015
			RU 2013157596	A	10-07-2015
			US 2014093442	A1	03-04-2014
			WO 2012166833	A1	06-12-2012
US 2010077739	A1	01-04-2010	NONE		
EP 2535102	A1	19-12-2012	CN 102869431	A	09-01-2013
			EP 2535102	A1	19-12-2012
			JP 5769708	B2	26-08-2015
			US 2012328499	A1	27-12-2012
			WO 2012002052	A1	05-01-2012
EP 2520354	A1	07-11-2012	CN 102869430	A	09-01-2013
			EP 2520354	A1	07-11-2012
			US 2013095013	A1	18-04-2013
			WO 2011162030	A1	29-12-2011