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Advanced exhaust gas aftertreatment systems for gasoline and diesel fuelled vehicles

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Abstract

In this article, the main reasons for the intensive development work being done on automotive emission control catalysts are discussed and the most important features of these technologies are described. Special attention is paid to the development of improved three-way catalysts for gasoline engines, that have to fulfil the more stringent future emission standards. Diesel fuelled vehicles and lean burn gasoline engines show completely different exhaust gas emission characteristics, which lead to dissimilar demands for the aftertreatment systems.

Keywords: Automotive emission control catalysts

1. Introduction

Motor vehicles provided mankind with a degree of freedom and mobility never known before and gave an important contribution to the development of our modern society. Hand in hand with the large scale production and use of motor vehicles people got aware of negative side-effects, as there are, e.g., pollutions, impacts on human health and on the climate. In the US, at any time being the country with the highest motor vehicle population and so realising these effects first, the growing knowledge of the impact of automotive emissions on the environment and the increasing environmental awareness of major parts of the public led to the introduction of emission control standards for motor vehicles starting at the sixties. This legislation led to reduced emissions of the major pollutants CO, hydrocarbons (HC) and NO_x per vehicle. However, due to the nearly linear increase of the worlds motor vehicle production — about 8 million/annual in 1950 to about 50 million/annual in 1990 [1] — the benefits for the environment were marginal. As a consequence, more stringent emission standards have been legislated not only in the US but also in other areas of the world, e.g., Japan and the European Community. Fig. 1 shows, as an example, the emission standards in the US for gasoline fuelled passenger cars from 1970 to 1997 as well as US and EC test cycles.

The emission standards are defined by a driving cycle in which the exhaust gas of a vehicle is collected and where the analysed emissions of CO, HC and NO_x may not exceed a value stipulated by the government. The emission standards are normally expressed as gram of emitted component per driven distance or per

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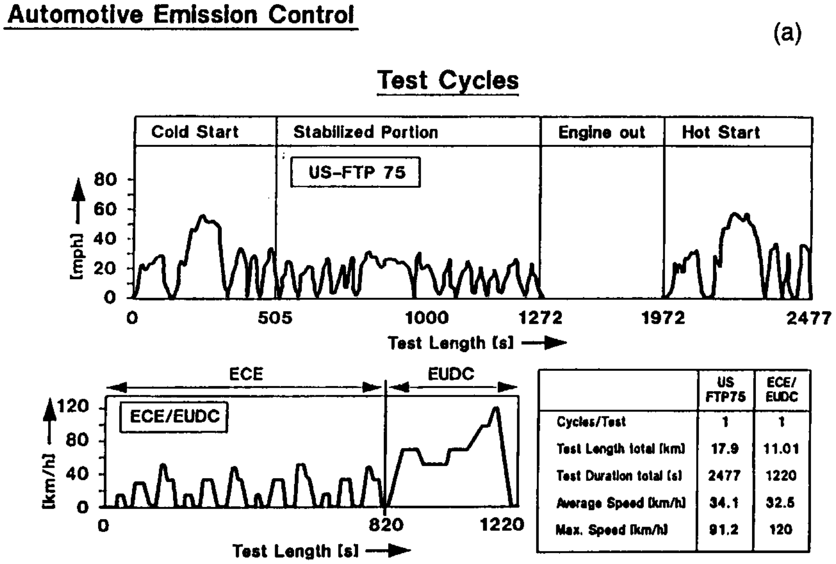
test. Whereas until 1975 most of the vehicles were able to meet the US-legislation by engine modifications, the more stringent emission limits from 1975 in conjunction with changes in the test cycle and the increasing durability requirements necessitated the introduction of precious metal based heterogeneous catalysts. Nowadays, state-of-the-art vehicle exhaust gas aftertreatment systems equipped with three-way catalysts can reduce the emissions of CO, HC and NO_x simultaneously by more than 90% per vehicle, see e.g. Ref. [2].

2. Catalytic exhaust gas aftertreatment of gasoline fuelled passenger cars

2.1. Past and present

As already discussed in former papers, the exhaust gas parameters for gasoline passenger



	US FTP75	ECE/ EUDC
Cycles/Test	1	1
Test Length total [km]	17.9	11.01
Test Duration total [s]	2477	1220
Average Speed [km/h]	34.1	32.5
Max. Speed [km/h]	91.2	120

US Gasoline Passenger Car Emission Standards 1970 to 1997 (b)

Year	Area	Pass Levels (g/mile)			Test Method
		CO	HC	NOx	
1970	Federal & California	23	2,2	-	7 Mode
1972	California Federal	39 39	3,2 3,4	3,2 -	FTP-72
1975	California Federal	9 16	0,9 1,5	2 3,1	FTP-75
1977	California Federal	9 15	0,41 1,5	1,5 2,0	
1980	California Federal	8 7	0,39 0,41	1 2	
1981	Federal & California	3,4	0,41	1	
1993	California Federal	3,4 7	0,26 0,41	0,4 1	
1994	California	3,4	0,125	0,4	
1997	California 25% of the fleet 2% of the fleet	 3,4 1,7	 0,075 0,040	 0,2 0,2	

Fig. 1. The development of US gasoline passenger car emission standards and US and EC test cycles.

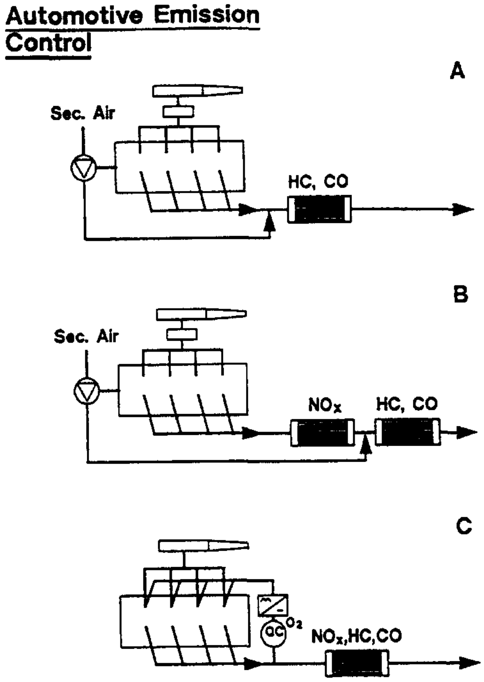


Fig. 2. Exhaust gas purification systems.

cars and so the reaction conditions are strongly dependent on the driving conditions, this being one of the major differences as compared to most of the catalyst applications known in chemical industry [3]. Nevertheless, it was possible to develop precious metal based catalyst technologies that could cope with these conditions. Dependent on the requirements three major purification systems can be classified (see Fig. 2):

Starting with the implementation of the legislation for modelyear 1975 vehicles in the US, most of the car manufacturers could not meet the standards for CO and HC by optimizing the engine management systems, while the NO_x targets in most cases could be met by introducing a fuel rich combustion. Therefore the use of a single bed oxidation catalyst in combination with the injection of secondary air in front of the converter was satisfactory, see Fig. 2A.

Further steps in legislation for modelyear 1977 also called for a reduction in the amount of NO_x. This could be achieved, e.g., by a double reactor system, schematically shown in Fig. 2B. Here, the exhaust gas of a fuel rich calibrated engine first passes a reduction and then an oxidation type catalyst. Between both systems, secondary air is injected to improve the oxidation of CO and HC. This process tolerates greater variations in the air–fuel ratio for the combustion but leads to high costs for a secondary air pump and two types of catalysts.

An alternative to this is given with Fig. 2C, where a multifunctional catalyst is introduced being able to convert CO, HC and NO_x simultaneously in the presence of a close-to stoichiometric exhaust gas. To guarantee this, the air–fuel mixture is regulated by a closed-loop control electronic injection system in combination with an oxygen sensor (also called lambda-sensor) that is needed to regulate the fuel injection system. Nowadays, these so-called three-way catalysts are predominant in exhaust gas aftertreatment devices.

The effectiveness of such a single-bed three-way catalyst is schematically shown in Fig. 3. In the excess of oxygen during combustion, i.e., air-to-fuel (A/F)-ratios > 14.6 or a so-called lean exhaust gas, the oxidation reactions for CO and HC are dominant, whereas under so-called rich exhaust gas conditions, i.e., excess of fuel or A/F-ratios < 14.6, the reduction of NO_x occurs with high conversion rates. Only in a very limited range of A/F being close to stoichiometry ($A/F = 14.6$), all three major

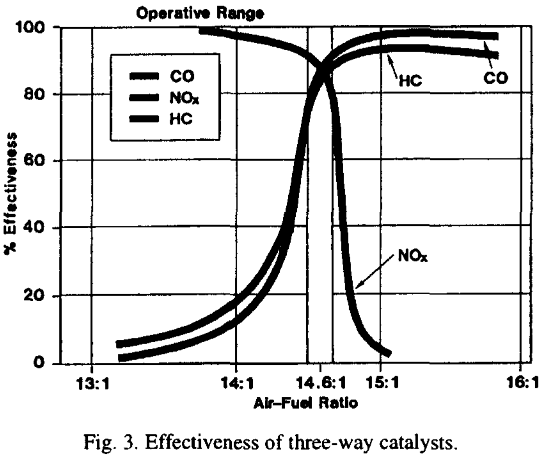


Fig. 3. Effectiveness of three-way catalysts.

pollutants are converted at high levels. The closed-loop engine management system described before must guarantee that the exhaust gas composition is kept within this so-called lambda-window [2,4].

The functional diagram of a monolithic type catalyst is shown in Fig. 4. Principally, three-way catalysts are structured as follows:

High porous layers of mixtures of different oxides, the so-called washcoat, are coated on monolithic ceramic or metallic substrates. The precious metals Pt, Pd and Rh needed to improve the activity and durability, are either impregnated after coating the washcoat or they are processed in one step together with the washcoat. As of today, the ceramic carrier material is dominant (about 90% of the total need), the use of pellet type catalysts rapidly declined over the last few years.

The major components of the washcoat systems are listed below:

- γ-alumina provides a large surface area for poison capture and improved precious metal dispersion. Alumina also improves the oxide-precious metal interactions resulting in favourable catalytic effects.

- cerium oxide and/or other rare earth oxides are mainly responsible for the oxygen storage/release characteristics of a catalyst. This reversible O_2 storage capacity mainly determines the width of the lambda-window to guarantee high three-way activity. Furthermore, ceria has a positive impact on the stability of the precious metal dispersion. However, an undesired side-effect of ceria is the possibility of increased H_2S-formation in the exhaust gas during the switch from lean to rich exhaust gas compositions as they typically occur during vehicle acceleration. Fig. 5 shows how the amount of ceria influences the activity of alumina/ceria washcoats being impregnated with Pt and Rh (mass ratio 5Pt/1Rh, 1.41 g/l; 400°C, SV = 50000 h^{-1}).

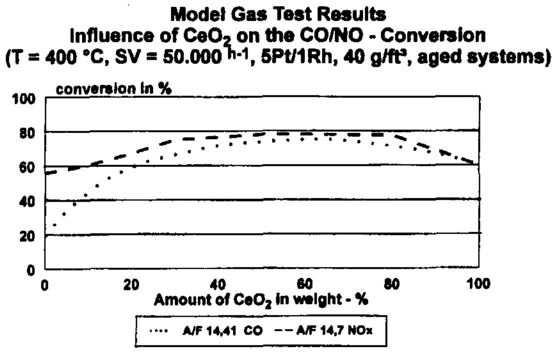


Fig. 5. Influence of ceriumoxide on the activity of Pt/Rh catalysts (model gas test, aged systems).

- other oxides like zirconium oxide increase the thermal stability of washcoats, or certain

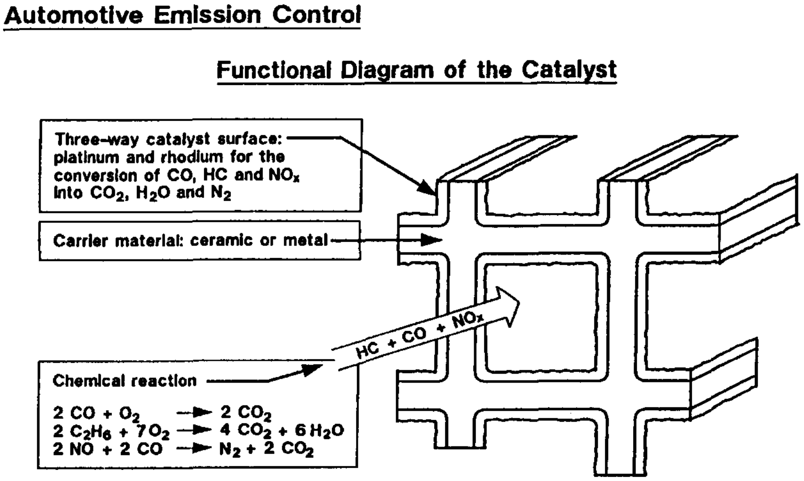


Fig. 4. Functional diagram of a catalyst.

additives being able to suppress the formation of H_2S, e.g., NiO, MnO_2 or Fe_2O_3.

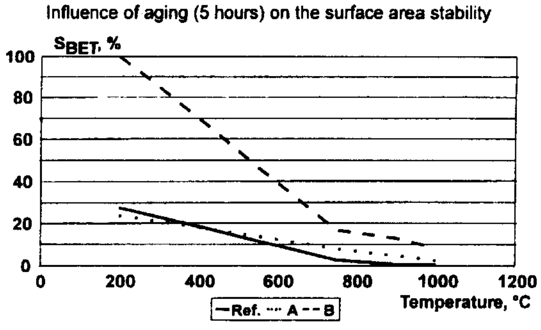
2.2. Outlines for future development work

Key factors which are gaining more and more importance in the field of three-way catalysts are the so-called light-off behaviour of the converter, i.e., the temperature at which a catalyst is able to convert CO, HC and NO_x effectively, as well as higher requirements concerning the durability. This becomes even more important taking into account that (a) in the test cycles, all starting at about 20°C, during the first 40 to 90 s generally more than 70% of the total emissions are set free [5] and (b) that the emission standards for modelyear 1994 and beyond demand a significant further reduction, especially for HC and NO_x in combination with an increased lifetime of the systems (see Fig. 1).

Different converter concepts have been discussed in the past to meet these requirements, e.g., electrically heated systems, burner systems, HC-adsorbers, special light-off catalysts and catalysts located closer to the engine [5–8]. At the moment there is a tendency that favours those concepts which locate the catalyst closer to the engine where the catalyst is exposed to higher temperatures — either as a special light-off or a closed-coupled main converter. Both of these solutions lead to a demand for washcoat systems with improved thermal stability in combination with an improved activity. To fulfil these targets new raw materials have been developed for improved washcoats as is shown in Fig. 6.

Fig. 7 gives the results of model gas and vehicle test (a) in which a reference catalyst was compared with a new developed washcoat impregnated with Pd/Rh (mass ratio 5Pt/1Rh, 1.41 g/l). From the model gas data, it is becoming clear that the new developed washcoat B leads to lower NO_x emissions during the switch from both rich to lean and lean to rich. Also a better conversion in the lean exhaust gas is recorded. However, the conversion of NO_x is higher when switching from rich to lean exhaust conditions as compared to the conversion going from lean to rich. This is a point that still needs to be improved.

(a) Modified Oxygen Storage Components



(b) Surface area stability of new developed washoats

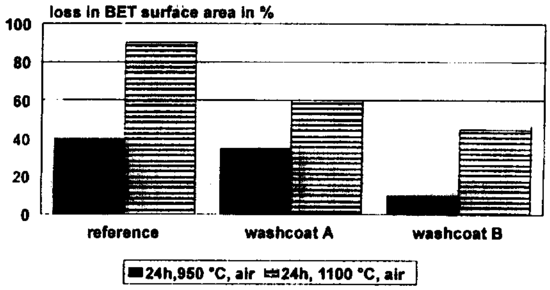
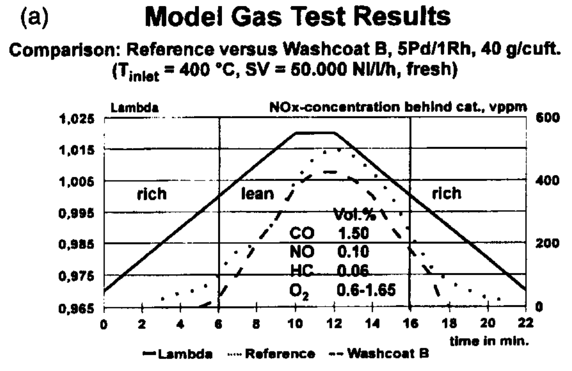


Fig. 6. Surface area stability of new developed washcoat materials and washcoat systems (top: oxygen storage component, bottom: complete washcoat).

Similar conclusions can be drawn from tests performed on two different vehicles with engine aged samples (Fig. 7b). With the new developed washcoat B for both vehicles, the emissions of CO, HC and NO_x could be reduced significantly, especially this is true for NO_x. The NO_x rest emissions where reduced by 50% for vehicle I of Fig. 7 that was operated with a small catalyst volume to engine displacement ratio of 0.8. For vehicle II, the advantages of washcoat type B are less pronounced, maybe due to the relatively large catalyst volume to engine displacement ratio of 1.3.

Future legislation in the US also demands the control of the catalyst activity during operation



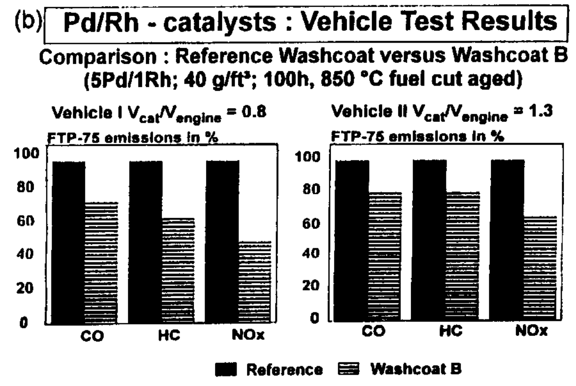


Fig. 7. Model Gas (top) and Vehicle Test Results (bottom).

conditions. According to this so-called on-board diagnosis principle a light in the driver's cabin will switch on in case of catalyst malfunction and the driver has to consult a garage for inspection and/or repair. As a physical measure to continuously determine the catalyst activity for HC, as it is proposed in the legislation, different concepts are discussed: e.g., to monitor the exotherm in the catalyst bed for certain driving conditions or to check continuously the OSC of the catalyst by means of a two lambda-sensor system, having one sensor located in front and one sensor behind the catalyst. At the moment, the OSC method dominates even though there is not a strong correlation between OSC and HC-conversion efficiency. As can be seen in Fig. 8, this is especially true for HC-conversions exceeding 80% [9,10].

In the case of catalytic converters being controlled by two lambda sensors, the kinetics of the oxygen storage and release must be adjusted to the engine management system to optimize the efficiency of the aftertreatment device. For this type of new requirements special experimental techniques have to be developed. Fig. 9 shows the first results of engine tests giving the A/F-ratio in front of and behind the catalyst. Apparently completely different behaviours can be realised for the two washcoats impregnated with Pt and Rh. To be able to fulfil future emission requirements, research has to be performed in which A/F-management, oxygen storage and release characteristics, catalyst activity, as well as complete converter stability have to be examined. Such a major task can

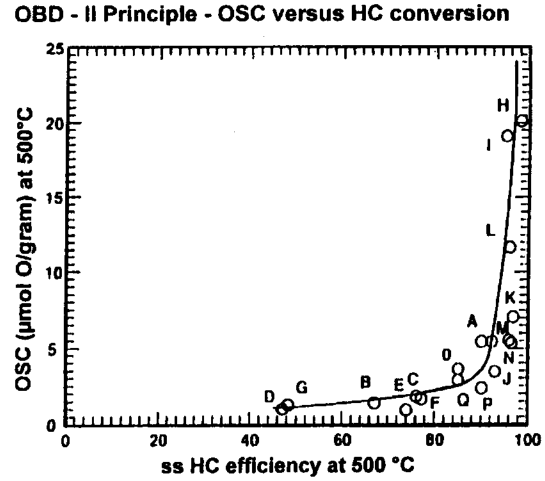


Fig. 8. Influence of the oxygen storage capacity on the performance of three-way catalysts [9].

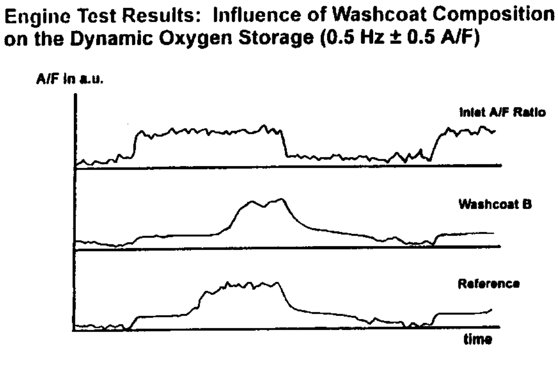


Fig. 9. Influence of washcoat composition on the oxygen storage and release results (0.5 Hz ± 0.5 A/F).

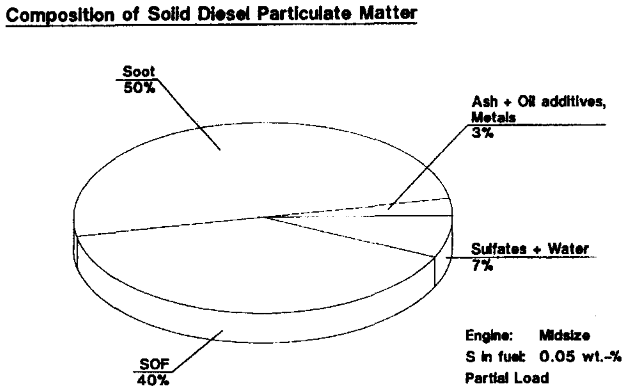


Fig. 10. Composition of diesel particulates.

only be successful if the forces of vehicle manufacturers and catalyst suppliers are joined.

3. Catalytic exhaust gas aftertreatment of diesel fuelled passenger cars

Additionally to the pollutants CO, HC and NO_x well-known from gasoline engines, the diesel exhaust gas contains components in the liquid and in addition the solid state, see Fig. 10 [11]. Regarding emission control special attention has to be paid to the solid portion, called particulates or particulate matter (PM).

The impact of diesel exhaust on the environment has numerous aspects which range from an obnoxious odour (caused amongst others by the oxygenates) or a coloured smoke (in which the condensed HC play an important role) and a general soiling of soot, to the suspected health hazard which is thought to be related to the PM. Although still a matter of debate, the particulates are suspected to have carcinogenic properties, which recent research attributes mainly to the solid carbon particle as well as to the slightly polar polynuclear aromatic components which can be adsorbed on the particulates.

Regarding the reaction conditions and comparing these to gasoline engines, diesel exhaust gas is characterized by high oxygen concentra-

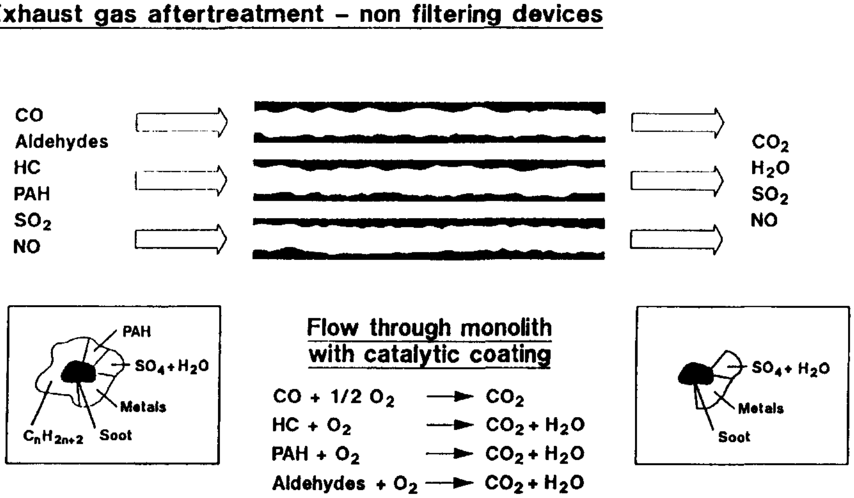


Fig. 11. Operation principle of a diesel oxidation catalyst.

tions, relatively low exhaust gas temperatures, high sulfur dioxide levels and the need for the catalyst to reduce PM [12].

3.1. Catalytic CO, HC and PM emission control by diesel oxidation catalysts

From the description above, it becomes clear that the reduction of tailpipe diesel emissions by catalytic exhaust gas aftertreatment is a complex phenomenon. The design of an engine and its operation characteristics considerably influences the composition, the properties and the amount of emissions. It is known that by a precious metal based oxidation catalyst CO and gaseous HC can easily be removed to a high extent since there is always excess of oxygen. Furthermore, it was also found that the newly developed diesel oxidation catalysts can also oxidize the liquid HC which are mainly adsorbed on the particles and are part of the PM and therefore reduce the amount of particulates even at the high sulfur dioxide levels present in the diesel exhaust. The operation principle of a diesel oxidation catalyst is shown in Fig. 11.

As can be learned from the vehicle test data shown in Fig. 12, the stability of those type of catalysts is excellent as there is no big difference in performance fresh and after 80000 km vehicle aging [13].

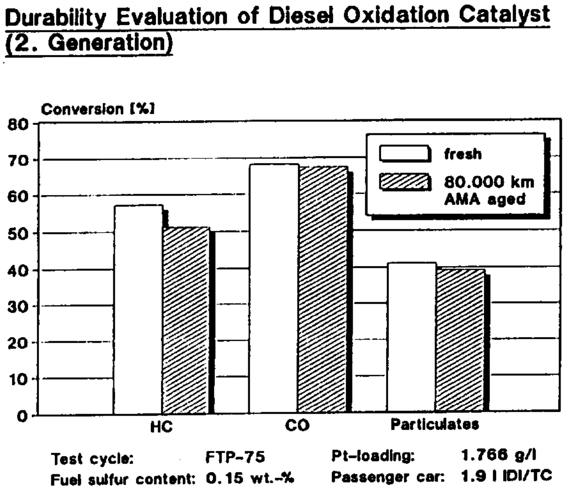


Fig. 12. Performance of diesel oxidation catalysts in vehicle tests.

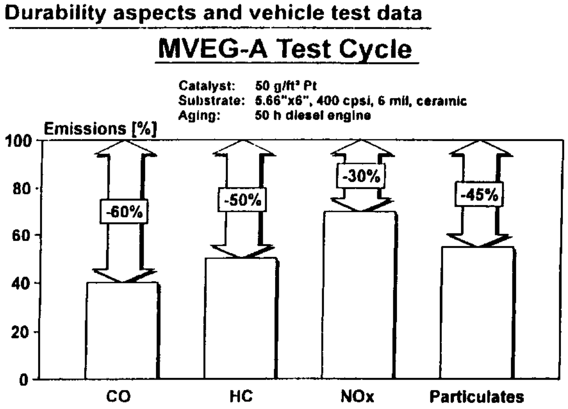


Fig. 13. Vehicle test results — the reduction of diesel engine emissions by a NO_x catalyst (EC test cycle, 50 h diesel engine aged, 1.766 g Pt/l).

3.2. Catalytic NO_x emission control by diesel NO_x catalysts

Whereas the diesel oxidation catalyst is a well accepted technology to reduce PM, CO and HC emissions in the exhaust gas of passenger cars in Europe as well as light and heavy duty trucks in the US, a major challenge left is the removal of NO_x from the oxygen rich exhaust gas of diesel engines. One possibility is the use of an exhaust gas recirculation system, leading to lower NO_x emissions but hand in hand an undesired increase of PM has to be noticed. Another approach focuses on the introduction of catalytic converters [14]. Unfortunately, conventional three-way catalysts do not convert nitrogen oxides under an excess of oxygen. With the selective catalytic reduction process by using ammonia as reducing agent, NO_x can be reduced under diesel engine exhaust gas conditions, but the use of nitrogen containing chemicals, like ammonia or urea, makes this process difficult to apply to on-road vehicles.

Catalysts for the selective reduction of NO_x by reducing agents were developed since several years [15]. The results of a preliminary vehicle test in the European MVEG-A test cycle

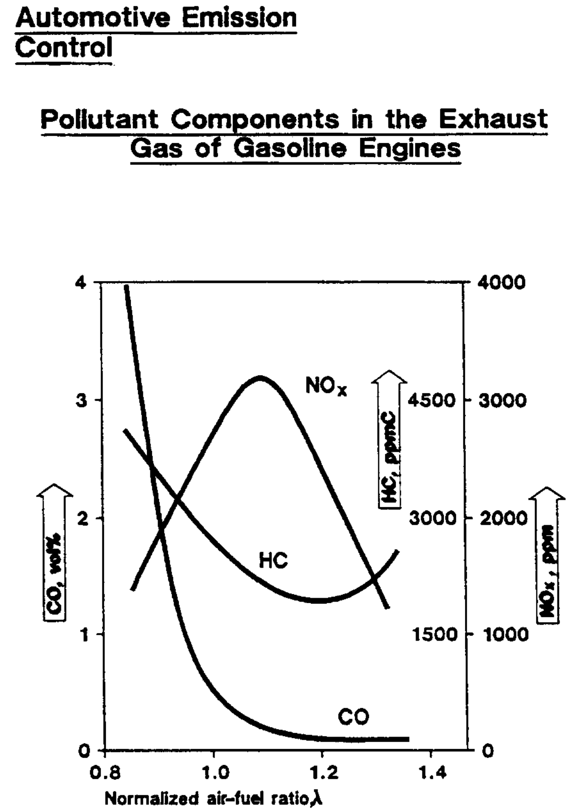


Fig. 14. The influence of the A/F ratio on the exhaust gas composition.

are shown in Fig. 13. The data show that NO_x reduction for diesel application is possible in combination with the oxidation of CO, HC and PM. But there is still a lot of development work needed to achieve higher conversion efficiencies for the pollutants. Again, this is a task which demands joined forces of vehicle and/or engine manufacturers and catalyst development groups.

4. Exhaust gas aftertreatment of lean burn engines

Another route to meet the new legislation is to leave the concept of the closed loop control of the spark ignition engine around the stoichiometric engine operation point. Indeed, as is shown in Fig. 14, the operation of a spark ignition gasoline engine above the stoichiometric point, which means under excess air, reduces the engine out emissions of CO, NO_x and up to some defined A/F-ratio, also of HC. The fuel consumption and therefore the CO_2 emission of the engine are decreased at the same time.

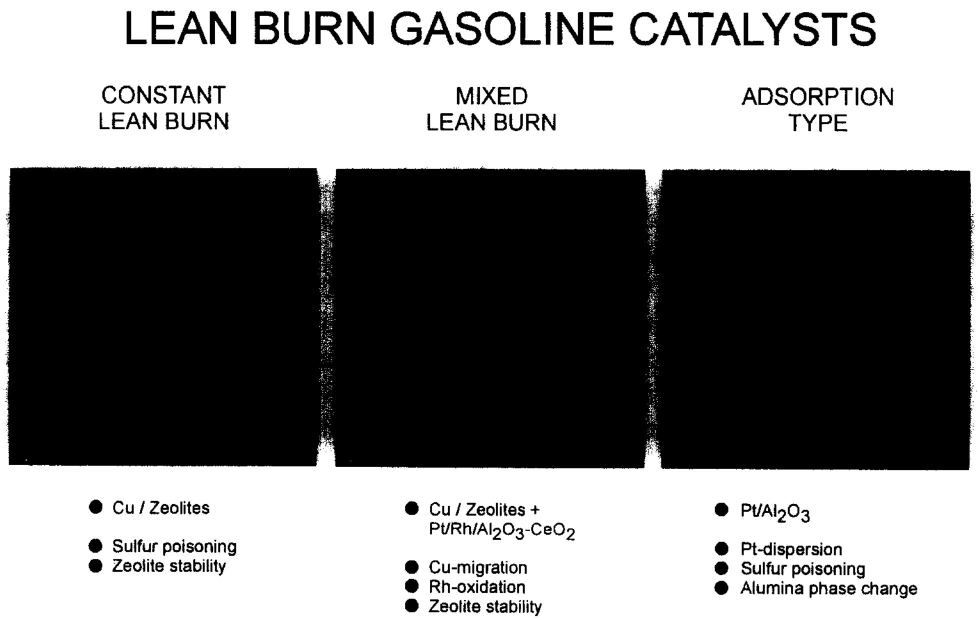


Fig. 15. Concepts for lean burn gasoline engines.

These lean burn engines still require exhaust gas aftertreatment, but the conversion level needed to meet the legislative requirements is somewhat lower as compared to the engines operated at the stoichiometric point. As of today, three types of lean burn engines are proposed — see Fig. 15. The first type is an engine that operates always in the lean burn range, with a lambda value in-between $\lambda = 1.5$ and 1.6. The exhaust gas composition will be net oxidizing at all vehicle driving conditions.

The second type is an engine that operates under some driving conditions in the lean burn mode and for other driving conditions in the stoichiometric mode. The latter operation conditions occur, for example, during acceleration of the vehicle.

Finally, the third type of engine also operates under both lean burn and stoichiometric conditions, the difference to the second type being that the operation mode does not depend upon the vehicle driving conditions, but is forced by the engine management system. Those engines will operate for a few minutes under lean burn conditions, after which the engine management system will adjust stoichiometric operation for a few seconds. Each of these engine types require a different catalytic aftertreatment system, as will be explained below.

With conventional three-way catalysts, a sufficient conversion level can be reached for CO and HC under the lean exhaust gas compositions of lean burn engines. However, three-way catalysts are unable to convert NO_x under these net oxidizing exhaust gas compositions. From intensive research programs, it was found that elements, such as Co and Cu, supported on some specific zeolites are able to convert the NO_x under lean burn conditions. Corresponding catalysts show some promise, although the durability, especially the high temperature stability and the resistance against sulfur poisoning, still needs improvement.

So, for the first and the second type of lean burn engines, catalytic aftertreatment systems are considered that include a Cu/Zeolite catalyst to convert NO_x under the lean burn conditions, and a conventional three-way catalyst to convert CO and HC, as well as NO_x under the stoichiometric operation conditions with the second engine type.

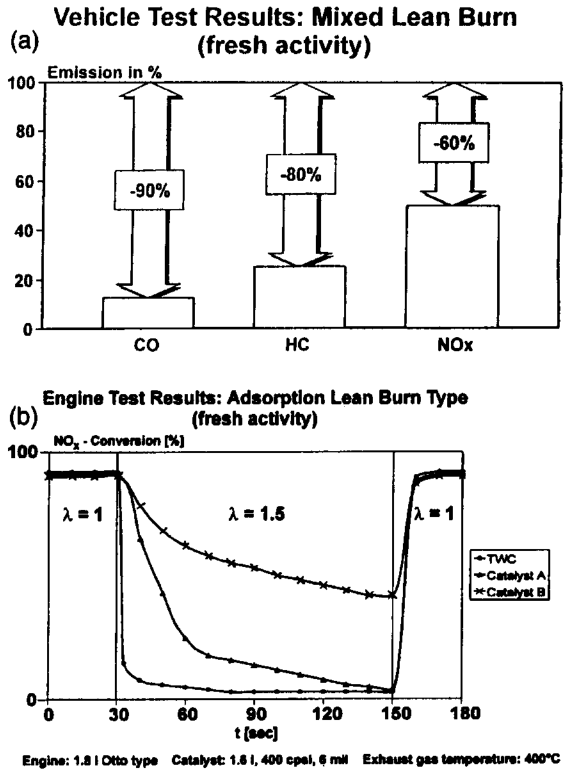


Fig. 16. (a) Mixed Lean Burn Concept, Vehicle Test Results (fresh converter), (b) Adsorption Type Lean Burn, Engine Test Data (fresh converter).

For the third type of lean burn engines, special catalysts are developed, which have the ability to convert NO to NO_2 and to store the NO_2 under the lean burn operation conditions. The stored NO_2 is reduced to N_2 once the engine is operated under stoichiometric conditions. The catalyst proposed in the patent literature for this application contains precious metals such as platinum, on three-way washcoats modified as to increase their capacity to store and release NO_2. Overviews are given in [16–19].

Fig. 16 shows the first results of vehicle and engine tests obtained with systems which were operated according to the mixed lean burn and the adsorption type concept. In both cases with the fresh systems, considerable NO_x conversions could be realised. The durability of these aftertreatment devices is under investigation right now.

5. Conclusions

The future more stringent emission standards still make it necessary to further improve the activity and durability of three-way catalysts even though per vehicle conversion rates of 90% or even more have already been reached for CO, HC and NO_x. Special emphasis must be placed on the development of improved washcoat components and a simultaneous engineering taking into account the interactions between catalyst formulation and engine-out emission behaviour. Furthermore, the reduction of NO_x in the lean exhaust gas of diesel as well as lean burn gasoline engines needs to be improved, necessitating amongst others, long-term fundamental research efforts from catalyst development groups. Again, this work has to be performed in close cooperation with engine and/or vehicle manufacturers to optimize the system efficiency.

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