CATALYTIC AUTOMOTIVE EXHAUST AFTERTREATMENT

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Abstract—Catalytic exhaust aftertreatment of vehicle engines is increasingly employed to the benefit of the atmosphere quality, especially in the large urban area of the world. Both spark-ignition and compression-ignition engines benefit from the application of catalytic converters for the elimination of their main pollutants. Catalysts are further employed in various forms as regeneration aids in particulate filters of diesel engines. The especially demanding exhaust gas conditions prevailing in each engine application pose challenging problems to the emissions control engineer. The attainment of strict emissions regulations requires highly active and durable catalysts, as well as optimized exhaust system design and engine controls. This paper reviews the potential of catalytic systems in automobile emission control. The review covers the catalyst technology applicable in each case, the operating principles and performance characteristics, durability aspects and considerations regarding the interactions between catalyst performance and engine management. The concise presentation of related mathematical model equations provides insight into the catalytic mechanisms and the physical phenomena involved. Further reductions of catalytically controlled automobile emissions may be attained by developing improved and more durable catalysts, by applying a systems approach in designing optimized engine–exhaust aftertreatment configurations, as well as by efficient control of in-use catalytic systems through inspection, maintenance and on-board diagnostics. © 1997 Elsevier Science Ltd.

Keywords: catalysis, chemical reactors, automobile, emission control.

CONTENTS

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NOMENCLATURE

3WCC	three way catalytic converter
A	reaction rate constant
A_f	filtration area of particulate filter
A/F	air to fuel mass ratio
ΔH	'combined' reaction enthalpy of soot oxidation (DPF), reaction enthalpy (3WCC)
$\Delta H_{(i)}$	specific heat of CO_2 formation (DPF)
$\Delta H_{(ii)}$	specific heat of CO formation (DPF)
c	species concentration
C_{p1}	specific heat capacity of soot deposit
C_{p2}	specific heat capacity of ceramic wall
C_{pg}	specific heat capacity of exhaust gas
D	hydraulic diameter of channel (DPF)
DPF	diesel particulate filter
E	apparent activation energy of soot oxidation
E_{ox}	activation energy for metal additive oxidation
E_{red}	activation energy for metal additive reduction
G	inhibition factor
h	convective heat transfer coefficient
H_{cond}	conductive heat flux (DPF)
H_{react}	reaction heat release (DPF)
k	collisions frequency factor (DPF)
k	mass transfer coefficient
K	adsorption equilibrium constant
k_1	rate coefficient for the soot combustion reaction
k_{ox}	rate coefficient for fuel additive (DPF) or oxygen storage component (3WCC) oxidation
k_p	permeability of ceramic substrate
k_{red}	rate coefficient for fuel additive (DPF) or oxygen storage component (3WCC) reduction
k_s	permeability of soot deposit layer
m	accumulated soot mass
M	molecular weight
M_c	atomic weight of deposit
M_{O_2}	molecular weight of exhaust gas
$\dot{N}$	exhaust gas molar flow rate
NEDC	new European driving cycle

OSC	oxygen storage capacity per unit reactor volume
p	exhaust gas pressure
R	reaction rate or gas constant
S	specific surface area per unit reactor volume
SOF	soluble organic fraction
S_p	specific area of deposit layer
t	time
T	temperature
v	exhaust gas velocity (DPF)
V_{cat}	catalyst volume
w	mass flux of exhaust gas per unit area (3WCC), thickness of the deposit layer (DPF)
w_s	channel wall thickness
y	oxygen concentration of the exhaust gas (DPF)
z	axial distance

Greek symbols

α	index for the completeness of soot oxidation
ϵ	void fraction
α_1	constant in channel pressure drop correlation
ΔP	filter backpressure
λ	thermal conductivity
μ	exhaust gas viscosity
ξ	concentration of catalyst in the soot layer (DPF), Eq. (23)
ρ	density
ψ	oxygen storage component oxidation fraction (3WCC), oxidation state of fuel additive in the deposit layer (DPF), Eq. (24)

Subscripts

g	exhaust gas
$i = 1, 2$	inlet, outlet channel
j	index for exhaust species
ox	oxidation
p	particulate layer
red	reduction
s	substrate
w	wall

Table 1. Operating conditions of catalytic converters (exhaust composition and exhaust gas temperatures) of different engine types

	CO (%)	HC (ppm C)	NO_x (ppm)	Particulate (g/kWh)	O_2 (%)	Redox	Temperature (°C)
Diesel	0.01–0.2	100–2000	200–1000	0.15–0.5	3–15	<1	80–700
Otto lean-burn	0.05–0.5	1000–5000	100–1000	—	0.5–5	<1	100–900
Otto	0.3–1	1000–5000	50–2500	—	0.1–0.5	1	150–1000
Otto CNG fuelled	0.1–0.5	1000–3000	50–2000	—	0.1–0.5	1	100–900

1. INTRODUCTION

1.1. Catalyst Operating Conditions in Engine Exhaust

Spark-ignition and diesel engines are a major source of urban air pollution. The spark-ignition engine exhaust gases contain oxides of nitrogen (NO and small amounts of NO_2—collectively referred to as NO_x), carbon monoxide (CO) and organic compounds, which are unburnt or partially burnt hydrocarbons (HC). Compression-ignition (diesel) engine exhaust contains smaller amounts of CO and HC, their main problem being the particulate emissions. The relative amounts depend on engine technology and operating conditions. Table 1 gives indicative values of the operating conditions for exhaust aftertreatment catalysts met in different technology engine types.

As shown in Table 1, in diesel engine exhausts, the concentrations of NO_x are comparable to those from SI engines. Diesel hydrocarbon emissions are, however, significantly lower than those from SI engines. The hydrocarbons in the exhaust may also condense to form white smoke during engine startup and warm-up. Specific hydrocarbon compounds in diesel engines exhaust are the source of characteristic diesel colour.

Diesel engines are also a source of particulate emissions. About 0.1–0.5% of the fuel is emitted as small particulates (0.1 μm mean size), which consist primarily of soot with some additional adsorbed hydrocarbon material. Carbon monoxide emissions of diesel engines are insignificant because of the abundancy of oxygen in diesel combustion.

Use of alcohol fuels in either of these engines substantially increases aldehyde emissions. Aldehydes would be another significant pollutant if these fuels were to be used in quantities comparable to gasoline and diesel.

Currently used fuels, gasoline and diesel, contain sulfur: gasoline in small amounts (<600 ppm weight S), diesel fuel in larger amounts (0.01–0.3% w.). In diesel engines the sulfur is oxidized to produce sulfur dioxide, SO_2, a fraction of which can be oxidized to sulfur trioxide, SO_3, which combines with water to form a sulfuric acid aerosol. In gasoline engines H_2S is produced in small amounts as a by-product of the reactions occurring in a 3WCC during oxygen deficiency conditions.

Improvements in engine design and fuel management have led to substantial lowering of raw emission figures during the last decades. Further reductions in exhaust emissions can be obtained by removing pollutants from the exhaust gases in the engine-exhaust system. Devices developed to achieve this result are usually assisted by catalysts, and include catalytic converters (oxidizing catalysts for HC, CO and SOF of HC, three-way catalysts for the simultaneous reduction of all three pollutants) and catalytically assisted traps or filters for the diesel particulate.

The temperature of exhaust gas in a warmed-up spark-ignition engine can vary from 300 to 400°C during idle, to about 1000°C in full load operation. Modern spark ignition engines usually operate at oscillating A/F, close to stoichiometric, as a result of the feedback lambda control system. The exhaust gas may therefore contain modest amounts of oxygen (when lean), or more substantial amounts of CO (when rich of stoichiometric). Lean burn engines, operating in the range $14.5 < A/F < 22$, are also produced in limited numbers, mainly in Japan. Diesel engines, on the other hand, operate significantly leaner, and load is controlled by the amount of fuel injected in a fairly constant (at constant speed) quantity of air. The diesel exhaust gas, therefore, contains substantial oxygen and is at lower temperatures (100–700°C). Removal of gaseous pollutants from exhaust after it leaves the engine cylinder can be either thermal or catalytic. However, thermal oxidation requires temperatures of the order of 600–700°C and high residence times of the order of 50 ms, and thus has limited applicability.[1]

Table 2 summarizes the application of various catalyst categories in different engine types to convert the regulated automobile pollutants, which will be reviewed in this paper. Catalytic oxidation of CO and hydrocarbons in the exhaust can be achieved at temperatures as low as 220°C. On the other hand, the only efficient methods known for the removal of NO from exhaust gas either at stoichiometric or lean A/F conditions, involve catalytic processes.[2] Consumption of NO by the reducing species present in the exhaust such as CO, hydrocarbons or H_2 is the preferred catalytic process. This is the case in 3WCCs for SI engines. NO_x reduction in oxygen rich conditions is currently achieved by catalysts which promote NO-hydrocarbons reactions in lean burn or diesel exhaust gas. In the latter case, additional amounts of hydrocarbons are usually injected in the exhaust gas to ensure high NO conversion efficiency.

Table 2. Application of catalysts in different technology engines

	Otto stoichiometric	Otto, lean-burn	Diesel
CO	3WCC*	Oxi-cat†	Oxi-cat
HC	3WCC	Oxi-cat	Oxi-cat
NO_x	3WCC	Lean NO_x‡	Lean NO_x
Particulate	—	—	Oxi-cat, Filter regeneration aids§

* Precious metal loaded three-way catalytic converters.
† Precious metal loaded oxidation catalysts.
‡ Zeolite based or precious metals catalysts for NO reduction.
§ Catalytically coated filters, fuel additives to lower filter regeneration temperature.

Particulates in the diesel exhaust gas stream may be removed by a particulate filter (trap). Due to the small particle size involved (order of $0.2\,\mu m$), mechanical filtration is the most effective trapping method. The accumulation of mass within the filter and the increase in exhaust manifold pressure during filter operation are major development problems. Diesel particulates, once trapped, can be burned up either by initiating oxidation within the filter with an external heat source, or by using a catalytically coated filter or, better, a fuel doped with some type of catalytic fuel additive. Reliable regeneration of diesel particulate filters remains a major challenge for diesel engine emission control.

1.2. Fuel Effects

The role of fuel composition and properties as an additional factor in reducing air pollutant emissions is widely recognized and discussed. In this discussion, two main streams are evident: improvement of the traditional fuels (reformulated fuels) and the introduction of alternative fuels. Improving traditional fuels has two different performance aspects:

1. To maintain engine and emissions control equipment in the best possible order during a vehicle's useful life. For example, sulfur in fuel can clearly affect the efficiency of catalyst conversion systems.
2. To further lower the engine out and, subsequently, catalyst out exhaust emissions.

The following parameters have been, and are being, studied extensively for their relationship with exhaust and evaporative emissions: aromatics content (clearly related to benzene emissions), olefins content (strong effect on butadiene emissions), benzene content, boiling range ($T50$, $T90$—significant effect on HC emissions), vapour pressure (high RVP leads to breakthrough of canister control systems) and content of oxygenated compounds (mainly lower CO emissions, MTBE may increase formaldehyde emissions).

Fuel improvements could enable the legislator to drastically reduce atmospheric concentrations of HC and (to a lesser extent) NO_x emissions. However, such issues should seriously consider the dual role of NO_x in ozone formation. In areas with low atmospheric HC–NO_x ratios, reducing NO_x can increase ozone

formation, whereas for high atmospheric HC–NO_x ratio areas, reducing NO_x decreases ozone.[3] In a recent U.S. study it was stated that in 2005 the light duty vehicles will contribute 5–9% of peak ground level O_3 values in three US cities. This contribution could be lowered by 25% by switching to reformulated gasoline. Afterwards the effect becomes appreciably smaller; also the effect strongly depends on the local pollutant mix.

Compressed natural gas (CNG) as a fuel for internal combustion engines is mainly composed of methane (from 60 to 99% by volume, depending on different sources). Although methane is a greenhouse gas, it does not contribute to the formation of photochemical smog and this is the reason that the U.S. legislation excludes methane from the regulated emissions. Thus, ULEV standards may be more easily attained by the use of CNG. However, if total hydrocarbon emissions are controlled, as in the EC legislation, special catalysts must be developed able to convert methane at relatively low temperatures.[4]

Liquified petroleum gas (LPG) has some advantages over gasoline regarding engine-out emissions which, however, essentially disappear with the introduction of the closed loop control three-way catalyst system.[5]

Methanol is used as a component of fuels for S.I. engines (M85 or M100). The main thrust behind California/U.S. interest in methanol is future transport energy supply and the potential for lowering photooxidants. Its use results in a clear reduction of HC emissions (of the order of 30–40%), less or no benzene emissions and acceptable methanol and formaldehyde concentrations in the air. Depending on the source material for methanol production, greenhouse gases can range from favorable or equal to, to very much worse than petrol. However, methanol fuelled vehicle exhaust also contains significant amounts of photochemically reactive aldehydes (primarily formaldehyde). Previous studies[6,7] have shown that maximum air quality benefit from methanol fuel can be obtained, provided that exhaust emissions of formaldehyde are kept to very low levels. The California Air Resources Board has enacted a 15 mg/mile formaldehyde emission standard for methanol-fuelled vehicles and the requirement that this standard be met for at least 5 years or 50,000 miles of vehicle use.
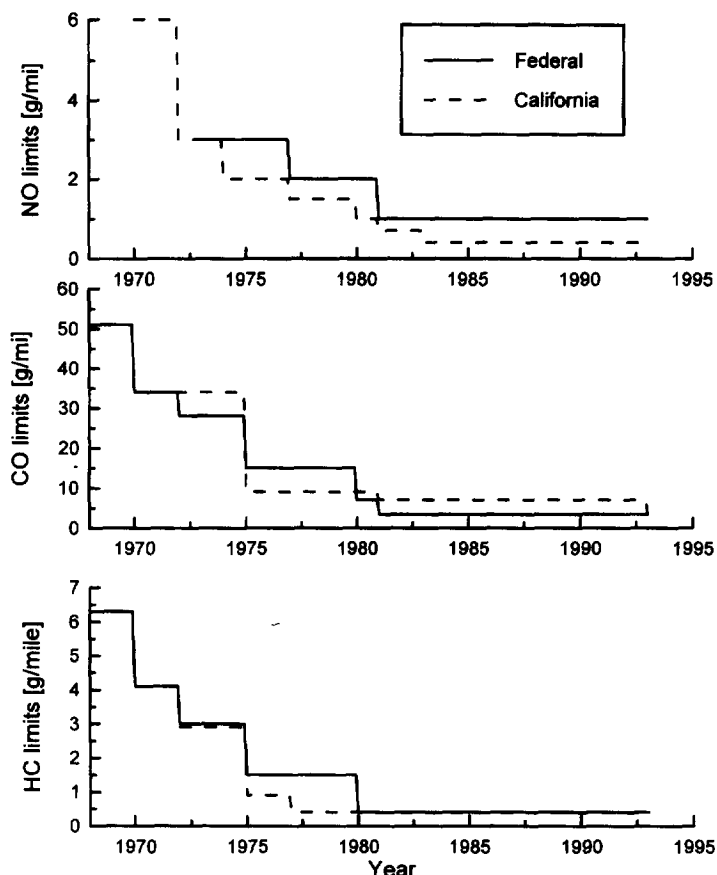
Fig. 1. Historical evolution of emission standards in the U.S. for light-duty vehicles.

Oxygenates, as a component of gasoline (MTBE or alcohol 10–17% or 3–4% O_2 equivalent), leads to lower CO emissions and somewhat lower HC including benzene. NO_x and acetaldehyde emissions can go up somewhat depending on the type of oxygenate, whereas evaporative emissions can go up strongly due to blocking of active carbon canister sites by alcohols.

Regarding the effect of diesel fuel on emissions, the following composition parameters have been, and are being, studied extensively for their relationship with exhaust emissions: density, cetane number and index, aromatics content, sulfur content, boiling range ($T50–T90$). In some studies an attempt has been made to differentiate between mono- and polyaromatics. Of all the fuel parameters, cetane number appears to be the only consistent parameter; it clearly affects the quantity and quality of particulate emissions in IDI and high speed DI engines. Rapeseed oil is discussed as a new agricultural product, that could replace other overproduced crops in Europe and elsewhere. In terms of regulated and unregulated emissions there appear to be major disadvantages for the straight oil. In esterified form (rapeseed oil methylester), small advantages in regulated emissions against increase of smell result. Like all vegetable oils, it offers an overall advantage in terms of CO_2 emissions. However, if the overall greenhouse gas emissions from the full production cycle of esterified rapeseed oil are considered, advantages over the diesel fuel cycle essentially disappear.

2. EMISSIONS LEGISLATION IN EUROPE AND THE U.S.

Figure 1 shows the evolution of U.S. emissions standards over the last 25 years. In the past, the exhaust emissions standards for passenger cars and other road vehicles were strengthened stepwise every few years. This concept was based on the experience that the manufacturers of passenger cars construct the vehicles in such a way that the emissions are lower than the limit values by a safety margin. The thus attainable emissions levels could then be considered as a new basis of common available technology, for the negotiations of the next step. This approach has an advantage for the manufacturer, since only small changes are required every 2 or 3 years. On the other hand, frequent modifications in the production had to be done and expenses for new certifications incurred. In the more recent EPA legislation, as well as in the European directive 94/12/EEC, it is required that the proposal for emission standards for passenger cars for the year 2000 should aim at a substantial pollutant reduction. For the following steps, the potential of the existing engine and exhaust

Table 3. Current and future emission standards for light-duty vehicles in the U.S. Implementation plan of the Clean Air Act Amendments

Emissions	Durability (miles)	MY 91 → (Tier 0) (U.S. 87)	MY 94 → (Tier I) (U.S. 94)	Proposal MY 2003 (Tier II)
HC	50,000	0.41	0.41	
NMHC	50,000		0.25	
	100,000		0.31	0.125
CO	50,000	3.4	3.4	
	100,000		4.2	1.7
CO (−7°C)	50,000		1.0	3.4
NO$_x$*	50,000	1.0	0.4	
	100,000		0.6	0.2
NO$_x$†	50,000	1.0	1.0	
	100,000		1.25	
Particulates	50,000	0.2	0.08	
	100,000		0.10	0.08

* Gasoline vehicles.
†Diesel vehicles.
Emissions figures in grams/mile.

Phase-in (%)	Model year										
	93	94	95	96	97	98	99	2000	2001	2002	2003
Exhaust emissions											
Tier I Phase-in		40	80	100							
Cold CO standard		40	80	100							
Tier II proposal											
In-use testing											
OBD II				100							
Cert. short test				100							
(CST)											
Enh. I/M (I/M 240)			30	100							
Testing procedures											
Revised FTP								Phase-in			
Rev. durability		old	old + alternative				new + alternative				
Others											
Clean fuel veh.											
fleets											

aftertreatment technologies must be reassessed from time to time.

Also, the effects of traffic induced CO$_2$ emissions must be taken into account in the evolution of emissions reduction technologies. In order to meet the aim of decreasing anthropogenic CO$_2$ emissions by 25% by the year 2005 compared to 1990, which was required by the German government during the 1st World Climate Conference in Berlin, a significant drop in traffic CO$_2$ emissions needs to be effected.

The properly working standard closed-loop TWC reduces emissions of HC, CO and NO$_x$ of a spark-ignition engine by 80–90%. The main potential to further reduce emissions is to reduce the time needed for the catalyst to reach light-off temperature. Currently, about 60–80% of total HC emissions over the New European Driving Cycle (NEDC) and the FTP 75 cycle are emitted within the first 200 sec of the cold start phase. As a large part of inner-urban driving is done over small distances (less than 3 km), the reduction of cold start emissions can significantly reduce the overall traffic induced immission burden.

Legislation in the U.S., especially California,

already requires much lower emission standards than can be achieved with the conventional TWC technology. Yet for Europe more stringent emission regulations are also scheduled, including a more realistic test procedure (e.g. omitting the 40 sec idle period at the beginning of the driving cycle), and new requirements regarding evaporative emissions and on-board diagnostics.

The basis for the new U.S. regulations are the 1990 Clean Air Act Amendments (CAAA), with the objective to improve air quality, particularly in large cities where in summer high ozone levels and in winter high CO levels are encountered. Besides tighter tail-pipe emission standards, the CAAA require the establishment of improved inspection–maintenance programmes, a reformulated gasoline program, legislation covering standards for vehicle fleet operators and for 'clean fuels–clean vehicles', which could lead to the introduction of alternative fuels.

Exhaust emissions standards defined in the CAAA are listed in Table 3. The current standard is Tier I which was phased in between 1994 and 1996, when certification up to 100,000 miles will also be required,
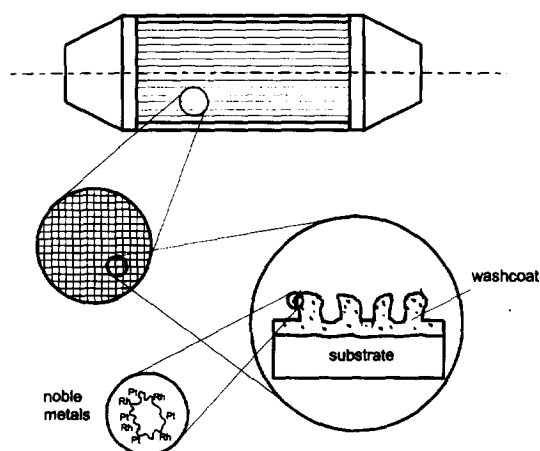
Fig. 2. Structure of the monolithic catalytic converter.

enforced by the possibility of an 'emission-recall'. Tier II standards will only come into effect if EPA decides that they are necessary, technically feasible and cost-effective.

More stringent emission standards are being introduced in California with the aim of progressively reducing vehicular emissions, to achieve the national air quality standards. In Table 3, the classes of low-emissions vehicles are also defined. Only the introduction of ZEV is mandatory, whereas for TLEV, LEV and ULEV implementation is up to the manufacturer, as long as his average NMOG fleet emissions are below the mandatory limits. Non-methane organic gases (NMOG) are the sum of NMHC (up to 12 C atoms) plus oxygenated compounds (up to 5 C atoms) such as aldehydes/ketones and alcohols (for alcohol-fuelled vehicles). The intention is to evaluate the tropospheric ozone formation potential, therefore methane is excluded, and the measured NMOG emissions are corrected using reactivity adjustment factors (RAF) which are basic characteristics for a given vehicle/fuel combination. For gasoline and alcohol vehicles additional tests are required at 10°C, with the same CO and NO_x standards, but less stringent NMOG and HCHO limits.

3. CATALYTIC CONVERTERS FOR STOICHIOMETRIC SPARK IGNITION ENGINES

3.1. Catalyst Types

The catalytic converters used in spark-ignition engines consist of an active catalytic material in a specially designed metal casing, which directs the exhaust gas flow through the catalyst bed. The active material employed for CO and HC oxidation or NO reduction (normally noble metals), must be distributed over a large surface area, so that the mass transfer characteristics between the gas phase and the active catalyst surface are sufficient to allow close to 100% conversion with high catalytic activity.[8] The most widespread type today employs a ceramic (or

metallic) honeycomb structure or monolith held in a metal can in the exhaust stream. The noble metals are impregnated into a highly porous alumina washcoat about 20–40 μm thick that is applied to the passageway walls (Fig. 2). A typical monolith has square cross section passageways with inside dimensions of the order of 1 mm separated by thin (0.1–0.15 mm) porous walls. The number of channels per square inch varies between 400 and 600,[9] although even higher cell densities of the order of 1200 cpsi have been demonstrated for metallic substrates.[10] The washcoat, 5–15% of the monolith weight is mainly composed of Al_2O_3 and has a surface area of 100–200 m^2/g.

The majority of the present day monolithic three way emission control catalysts for gasoline engines use a combination of platinum and rhodium as precious metal components. There has been a keen interest lately in replacing a part or all of the platinum content of an automotive catalyst by palladium, mainly as a means to reduce the precious metal cost of the catalyst.[11] Most of the oxidation catalysts used in the U.S.A. on model years 1975–1980 vehicles, contained Pt and Pd in the ratio 5 Pt–2 Pd at a typical loading of 50–70 g/ft³. Also, a lot of the bead type three way catalysts used by General Motors on model year 1981–1992 vehicles, used Pt together with Pd and Rh. In the literature, precious metal loading ranges are reported for Pt 30–100 g/ft³; Pd 0–120 g/ft³; and Rh 5–10 g/ft³. The ratio of Pt to Pd was in most cases higher than one. During the development of these catalysts it was recognized that each of the three precious metals Pt, Pd and Rh need a particular position in the catalyst to function properly. To this end, advanced impregnation techniques were developed. A number of disadvantages have been reported when Pd is incorporated in Pt–Rh catalysts. For example it has been demonstrated that Pd can form alloys with Rh in which Pd is enriched at the alloy surface, thereby suppressing the full deployment of the excellent catalytic activity of Rh.[12] To avoid this, advanced, costly impregnation technologies are necessary.

In addition, several fundamental studies have shown that the resistance of Pd against poisoning by for example lead and sulfur is substantially inferior to that of both Pt and Rh. It was shown that sulfur decreases, in particular, the ability of Pd to convert CO and HC in net reducing exhaust gas conditions, thereby narrowing the A/F window, in which a high conversion of CO, HC and NO_x is simultaneously reached.[11] The same studies, however, stressed that this negative influence does not occur in net oxidizing exhaust gas composition. Other studies showed that with net oxidizing conditions, Pd favours the $CO–O_2$ reaction more than the CO–NO reaction—as opposed to Rh—so that the A/F window is narrowed by the poorer NO_x conversion at the lean side, when using Pd.[13]

Finally, Pd only catalysts have been used in specific applications (e.g. as pre catalysts etc.). However, it is recognized that only Rh provides selective reduction

of the nitric oxide to nitrogen with low ammonia formation. Muraki et al.[14] demonstrated that under reducing conditions with Pd catalysts, poor NO_x reduction results. The reduction of nitric oxides on Pd catalysts was found to be significantly inhibited by hydrocarbons.[15] The light-off performance and NO_x reduction efficiency have been improved by both periodic operation and addition of lanthanium to the catalyst.[16,17]

The net result of these technical facts is that the successful use of Pd in three way emission control catalysts was limited to applications where the engineering targets for the conversion of CO, HC and NO_x are lower than 90% and/or where the content of the catalyst poisoning elements in the fuel is low—such as the gasoline available on the Japanese market.[18] In 1992 only about 9% of the Pd supplied to the market found use in automotive catalysts, compared to 45% for the platinum and 85% of the rhodium. Recent trends in improvement of the catalyst relevant properties of the fuels available in the U.S. and Europe, along with the wide application of advanced engine management systems with a capability for much tighter A/F control close to stoichiometry, relieve the above-mentioned constraints to the use of Tri-metal catalysts.[11,19] In addition, the significant advantage of Pd in producing faster catalyst light off under net oxidizing conditions is exploited by means of introducing Pd-based light-off catalysts, which lead to significant further reduction of cold start emissions. Also, the development of advanced washcoats for Pd compensated to some extent, some of the disadvantages mentioned above.

Apart from the precious metals, the 3WCC alumina washcoat also contains other components, which function as catalytic promoters or stabilizers against ageing. Cerium is normally present in high quantities in the washcoat (order of 30% w. or $1000 \, g/ft^3$) and has multiple functions: stabilization of the washcoat layer and improvement of thermal resistance, enhancement of precious metal catalytic activity, promotion of the water–gas shift reaction and function as an oxygen storage component.[20-22] Iridium has remarkable activity for NO reduction under net oxidising conditions.[23] However, the availability of Ir is lower than Rh and it tends to form volatile oxides in the exhaust environment, so it is not used in automotive catalysts. Ruthenium and nickel have catalytic properties for NO reduction. Nickel is also capable of suppressing H_2S formation. They are not currently used as stand-alone catalysts, but are potential additives for catalytic washcoats.

3.2. Phenomena Involved in 3WCC Operation

3.2.1. Heat and mass transfer

Although the flow in the exhaust piping of an engine is normally turbulent, the Reynolds (Re) numbers in the converter monolith channels are in the laminar region ($20 < Re < 300$). The transition of the flow to laminar occurs in the first few millimeters after the monolith entrance, where the transport phenomena are generally enhanced.

The main heat transfer mode in the converter is the convective heat exchange between the exhaust gas and the substrate. Heat is additionally generated from the exothermic reactions of some exhaust components (CO, hydrocarbons) on the catalytic washcoat. In the case of electrically heat catalysts, electrical energy is supplied to the substrate in order to quicken its temperature rise during warm-ups. At high operation temperatures, heat radiation from the substrate to the surrounding walls become appreciable. Related studies[24] have shown that the latter effect is generally of secondary importance. The converter heat losses to the ambient occur via convection (free and forced) and radiation from the converter shell.

The concentration gradients between the flowing gas and the reactive washcoat induce the convective mass transfer in the monolith channels. Since the species of interest are present in low concentrations in the exhaust gas of a gasoline engine, the mass transfer is governed by the laws of diffusion in dilute mixtures and the analogies between heat and mass transfer are fully applicable.[25]
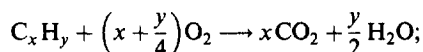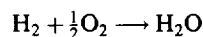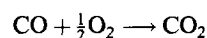
3.2.2. Inlet flow distribution

Non-uniformities in the velocity field at the inlet of the converter may cause both poor converter performance, due to localized high space velocities, and increased ageing, due to poison accumulation in high mass flow rate areas of the monolith.[26,27] Consequently, a large amount of computation and experimental work has been conducted so far, aiming at the minimization of the flow maldistribution.[28,29] An outcome of these studies is related to the quantification of maldistribution by means of semi-empirical indices, which correlate well with the flow Re numbers and the geometrical parameters of the diffuser and monolith.
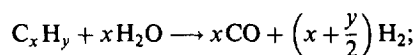
3.2.3. Reactions

The main reactions contributing to the conversion of the main SI engine pollutants, that take place in a three way catalytic converter are:

oxidation reactions

$$CO + \tfrac{1}{2}O_2 \longrightarrow CO_2$$
$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O$$
$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O;$$

steam reforming

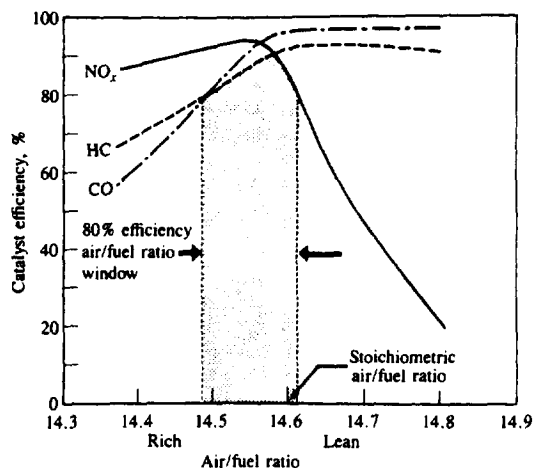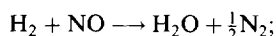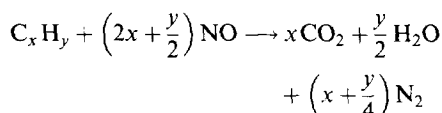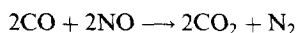$$C_xH_y + xH_2O \longrightarrow xCO + \left(x + \frac{y}{2}\right)H_2;$$

Fig. 3. Conversion efficiency of NO, CO and HC as function of the air–fuel ratio in a three way catalytic converter.[8]

NO$_x$ reduction

$$2CO + 2NO \longrightarrow 2CO_2 + N_2$$

$$C_x H_y + \left(2x + \frac{y}{2}\right) NO \longrightarrow x CO_2 + \frac{y}{2} H_2O$$

$$+ \left(x + \frac{y}{4}\right) N_2$$

$$H_2 + NO \longrightarrow H_2O + \tfrac{1}{2} N_2;$$

water–gas shift

$$CO + H_2O \longrightarrow CO_2 + H_2.$$

If an engine is operated at all times with an air–fuel ratio at or close to stoichiometry, NO reduction, CO and HC oxidation can be attained in a single catalyst bed. Enough reducing gases will be present to reduce NO, and enough O$_2$ to oxidize the CO and hydrocarbons. Such a catalyst is called a three way catalyst, since it removes all three pollutants simultaneously. Figure 3 shows the conversion efficiency of NO, CO and HC as function of the air–fuel ratio. There is a narrow range of air–fuel ratios near stoichiometry in which high conversion efficiencies for all three pollutants are achieved. The width of this window is narrow, about 0.1 air–fuel ratios for catalyst with high mileage use, and depends on catalyst formulation and engine operating conditions.[8]

This window is sufficiently narrow to require the application of closed loop fuel injection control. An oxygen sensor in the exhaust is used to indicate whether the engine is operating on the rich or lean side of stoichiometry, and provide a signal for adjusting the fuel system to achieve the desired air–fuel mixture. Holding the equivalence ratio precisely on the chosen near-stoichiometric value is not a practical expectation of the state-of-the-art feedback systems, and the equivalence ratio oscillates around the set point in an approximately periodic manner as the fuel flow is varied. Experimental data show that there is a considerable widening of the air–fuel ratio window, where all three pollutants are effectively removed,

with cyclic variation of the fuel flow.[30] The maximum conversion efficiency in the middle of the window is reduced, however, from its value when there are fluctuations. A number of researchers addressed the problem of optimum electronic control of A/F fluctuation characteristics (setpoint, frequency, amplitude) for A/F window maximization.[31] On the other hand, significant research activities are aimed at exploiting the capabilities of model based A/F control in eliminating deviations from stoichiometry, especially during transient operation.[32,33]

Because of the cyclic variations in exhaust gas composition about a set point close to stoichiometry, it is desirable that the catalyst is able to reduce NO even when there is a slight excess of oxygen (on the lean side) and remove CO and HC when a slight deficiency of oxygen is present (on the rich side). Rhodium is the principal ingredient used in commercial catalysts to convert NO. It is very active for NO reduction, is much less inhibited by CO and sulfur compounds, and produces less NH$_3$ than Pt. To remove NO under slightly lean conditions, the catalyst must react the CO, H$_2$ or HC with NO rather than with O$_2$, as the exhaust gas passes through the catalyst bed. Rhodium shows some NO reduction activity slightly lean of stoichiometric. On the rich side, the three-way catalyst window is determined by hydrocarbon and CO removal. Platinum is most commonly used for HC and CO oxidation; it has good activity under stoichiometric and lean conditions. When sufficient rhodium is present, the participation of Pt in NO removal is minimal. In the rich regime, the three-way catalyst consumes all the oxygen that is present in the exhaust, and as a consequence removes an equivalent amount of CO, H$_2$ and hydrocarbons; H$_2$ is the most reactive among the three species by itself; in the presence of CO it tends to light-off at the same time as the other species.

The water–gas shift reaction and the steam reforming reaction can additionally consume CO and HC, respectively.[34] The exhaust contains an H$_2$/CO ratio of about 1/3, where the equilibrium ratio at 500°C is about 4. Considerable CO removal can be expected if the water–gas shift equilibrium is approached. Platinum is active in promoting this reaction, but is strongly poisoned by sulfur.[35] For large molecular weight paraffin hydrocarbons and for olefins and aromatic hydrocarbons, the equilibrium for the steam-reforming reactions lies to the right. This reaction can therefore lead to considerable hydrocarbon removal. Rhodium is particularly active in the steam-reforming reaction.

3.2.4. Chemical kinetics

The multitude of the heterogeneous reactions taking place on the catalytic washcoat poses a challenge for the engineer involved in the design, modeling and manufacturing of three-way catalytic converters. Converter models require reliable kinetic

expressions that account for the composition and temperature dependence of the reaction rates. The kinetic expressions should be conveniently formed in order to allow flexibility in matching behavior of a large variety of catalyst formulations and washcoats.

In the classical work of Voltz et al.,[36] extensive measurements on pellet-type Pt catalysts are processed to derive kinetic rate expressions for the oxidation reactions of CO and C_3H_6 under oxygen rich conditions. These relations are of the Langmuir–Hinshelwood type and account for the inhibition of CO, C_3H_6 and NO. According to this theory, the inhibition is essentially governed by the adsorption characteristics at equilibrium without reaction. Consequently, measurements of adsorption isotherms under non-reacting conditions, yield in principle the adsorption constants involved in an L–H expression. In practice, Voltz et al.[36] used a numerical integration–optimization computer program to find the best combination of kinetic parameters for a given set of rate equations of this type.

Due to the absence of analogous works for other types of catalysts, the above mentioned rate expressions—with minor modifications—have been extensively used by the majority of researchers. Proceeding further towards the case of a three-way catalyst, the first rate expressions concerning the simultaneous oxidation of CO and reduction of NO were provided by Subramanian and Varma.[37] Here, again, the expressions are of the Langmuir–Hinshelwood type, but they also involve fractional and positive orders which are of empirical nature. Montreuil et al.[38] present a methodology to tune a mathematical model in order to best represent the steady-state conversion characteristics of Pt–Rh and Pd–Rh catalysts under selected redox and temperature conditions. This methodology involved 13 reactions and 97 independent tunable parameters for the kinetic rate expressions.

Most of the recent mathematical models rely on the Langmuir–Hinshelwood type expressions of Voltz et al.[36] for the CO and hydrocarbons oxidation, with modified activation energies and activity factors, best suited to the activity of the catalyst modeled. It appears that this approach is acceptable, since it provides the required accuracy levels, at least under the operating conditions met in the most common automobile applications.[39]

The reaction mechanisms involved in NO reduction are more complicated. Oh[20] studied the reaction of CO–NO on a Rh catalyst and derived activation energies and reaction orders for a variety of washcoat supports under CO excess (rich) conditions. In order to extend this kinetics data to the lean region, one may refer to Koberstein and Wannemacher,[40] who presented a series of measured rate data regarding the CO–NO reaction in binary mixtures and in the presence of O_2 on a Pt–Rh catalyst. At relatively high temperatures (above 400°C) an apparent first-order
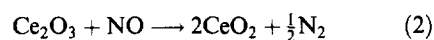
kinetic for CO is found, until complete consumption of one reaction partner near the surface enforces an approximately zero order kinetic. In fact, due to additional inhibition of the reaction, a slightly negative order is identified, which is in agreement with the findings of Oh.[20]

3.2.5. Oxygen storage

In most current technology gasoline cars the signal of the lambda sensor[41] is used as a feedback control signal for the fuel injection system in order to ensure that a stoichiometric fuel–air mixture is supplied in the cylinders. However, the system's response lag (mainly attributed to the exhaust gas travel time and the sensor's response delay) causes the air-to-fuel ratio to oscillate around the stoichiometric value with the limit cycle frequency of the control system. In some modern fuel injection systems, the A/F ratio is oscillated deliberately by the engine management electronic control unit. The behavior of the 3WCC under such dynamic conditions is of high practical interest.

The conversions of NO, CO and hydrocarbons in a three-way catalyst, operated with cyclical variations in the equivalence ratio, are larger than estimates based on summation of steady-state values during the cycle. At least part of the improved performance is thought to be due to the ability of the catalyst to undergo reduction–oxidation reactions.[42,43] Such a catalyst component is usually referred to as an oxygen storage component. In its oxidized state it can provide oxygen for CO and hydrocarbon oxidation in a rich exhaust-gas environment, and in the process be reduced. When the exhaust cycles to lean conditions, this reduced component can adsorb O_2 or NO (which removes NO directly or indirectly by reducing the O_2 concentration). The oxidized component can, in turn, provide oxygen for CO and HC oxidation in the next rich cycle. Components such as CeO_2 or ReO_2 which exhibit this redox behaviour are included in the washcoat of commercial three-way catalysts.[44–46]

The classical experimental studies of Herz[42] showed that oxygen adsorption and desorption phenomena, under periodically varying inlet conditions, are attributed to the presence of cerium and, to a much lesser extent, other washcoat species. The function of cerium as oxygen storage component is based on its ability to form both 3- and 4-valent oxides. Under net oxidizing conditions the following Ce oxide reactions may take place:

$$Ce_2O_3 + \tfrac{1}{2}O_2 \longrightarrow 2CeO_2 \qquad (1)$$

$$Ce_2O_3 + NO \longrightarrow 2CeO_2 + \tfrac{1}{2}N_2 \qquad (2)$$

$$Ce_2O_3 + H_2O \longrightarrow 2CeO_2 + H_2. \qquad (3)$$

On the other hand the CeO_2 may function as an oxidizing agent of the exhaust-gas species under net reducing conditions according to the following
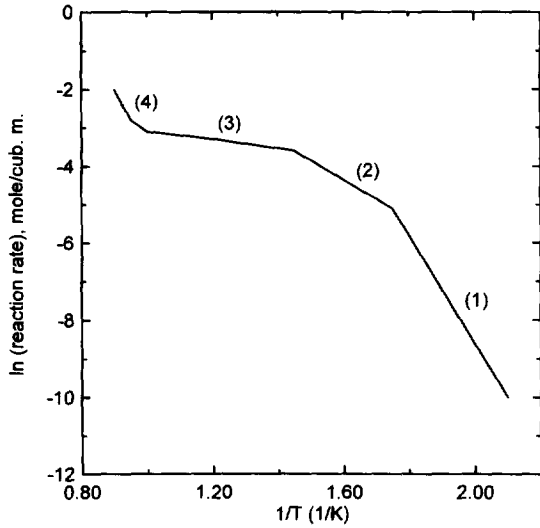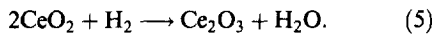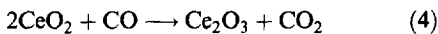
Fig. 4. Reaction rate measurements (Arrhenius plot) of $CO-O_2$ reaction in a Pt–Rh catalyst.[40]

reactions:

$$2CeO_2 + CO \longrightarrow Ce_2O_3 + CO_2 \qquad (4)$$

$$2CeO_2 + H_2 \longrightarrow Ce_2O_3 + H_2O. \qquad (5)$$

The interaction of Ce oxides with the hydrocarbons has been reported to be of minor importance.[42] The oxygen storage availability is apparently a function of the washcoat Ce content and dispersion. Moreover, the stored oxygen available to react under operating conditions is a function of the local temperature and redox environment.[47]

3.3. Catalyst Activity Assessment

3.3.1. Light-off tests with mini scale catalysts

The activity of the catalyst as a function of its temperature is a critical feature of its performance and is affected by a number of exothermic reactions. Arrhenius plots, derived from dedicated measurements, yield information regarding the reaction kinetics of single reactions. Figure 4 presents, as an example, a typical Arrhenius plot obtained for the $CO-O_2$ reaction on a Pt–Rh catalyst.[40] Four temperature regions characterized by their own activation energy may be recognized in this plot. In the first the overall reaction is controlled by the reaction kinetics, whereas in the second the conversion is limited by the pore diffusion in the alumina washcoat. The third region corresponds to mass-transfer controlled conditions and in the fourth, high temperature region the homogeneous reaction becomes the controlling phenomenon.

An easier way to assess the catalytic activity in the laboratory is to measure the efficiency with which hydrocarbons, carbon monoxide and nitrogen oxides, contained in synthetic exhaust gas, are converted as functions of catalyst temperature. Such tests are performed on a monolithic catalyst core or representative
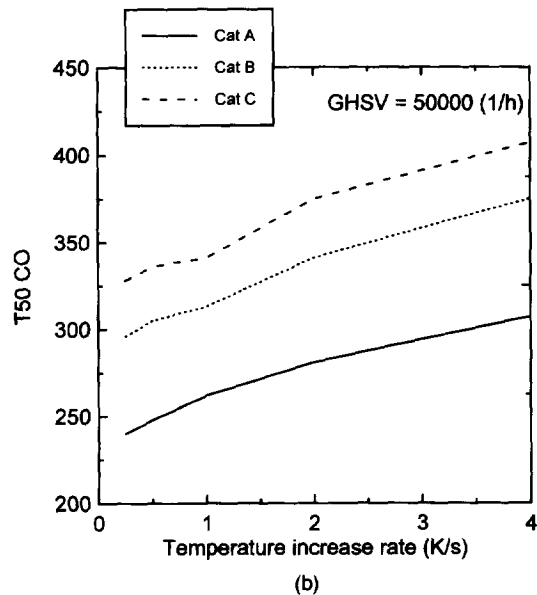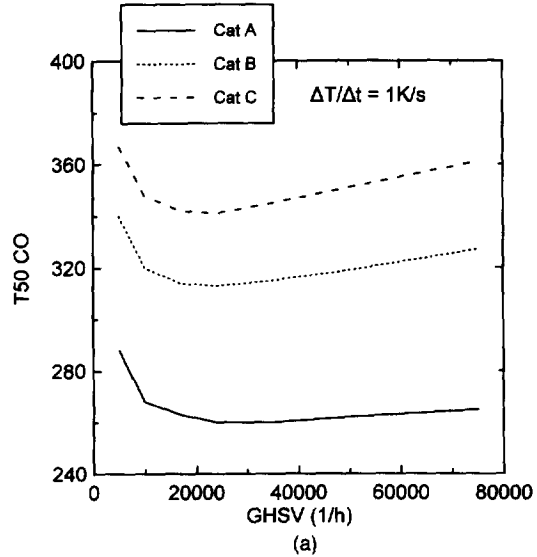

Fig. 5. The dependence of the observed light-off temperature for 50% CO conversion on (a) the GHSV; and (b) the temperature increase rate in a light-off test.[50]

pellet sample aged in a predetermined way. The sample is subjected to a representative flow of synthetic gases to simulate car operating conditions. The temperature of the mixture is controlled to increase at a specified rate. The conversion efficiency is measured by the composition upstream and downstream of the converter as a function of inlet gas temperature. The composition of the synthetic gas mixture can optionally be lean, rich or modulated around a mean concentration at a specified amplitude and frequency. The latter option is used to better reproduce the catalyst operation under real world conditions on an engine operating with closed loop lambda control.

The main light-off test parameters (feed-gas space velocity, temperature increase rate) should be
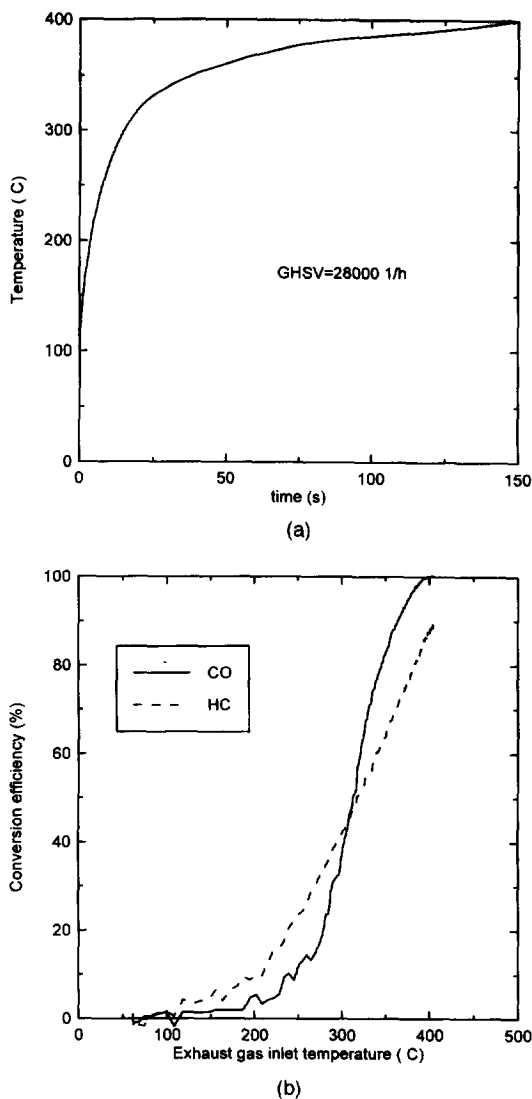
Fig. 6. (a) Exhaust gas temperature and (b) converter efficiency observed in a full-scale light-off test conducted on an engine test bench. GHSV = 28,000/hr, $A/F = 14.85$, 2.1 l catalyst—Pt–Rh 5:1—50 g/ft^3.[39]

carefully selected, in order to best exploit the measurement results.[48] More specifically, a well designed light-off test should be able to provide a clear differentiation in the light-off temperature among activity catalysts. Mathematical models have been used to optimize the design of a light-off test in this sense.[49,50]

Figure 5 (a) shows the dependence of the 'observed' light-off temperature for four different activity catalysts when the test is performed with variable space velocities. The temperature increase rate for these simulations is 1 K/sec. For all catalysts, a remarkable increase in the light-off temperature is recognized for GHSV values below 20,000/hr, where a local minimum is observed. For GHSV greater than 20,000/hr the light-off temperature increase is more profound for the lower activity catalyst. Similar investigations may be performed regarding the effect

of the temperature increase rate selected for such a test procedure. Figure 5 (b) presents, in the same manner, the differences in the light-off temperature measured for different test conditions. Clearly, the temperature corresponding to 50% conversion is strongly dependent on the temperature increase rate.[50]

The tendencies observed in these results are explained by the effects of catalyst substrate warm-up behavior during the light-off test. In general, the temperature of the catalyst sample is axially non-uniform during the test; on the other hand the exhaust gas inlet temperature is not necessarily a sufficient representation of the catalyst temperature. The use of the mean value of exhaust-gas inlet and outlet temperatures to correlate the catalyst performance has been shown to be more representative for a wide range of test conditions. More details on the analysis of light-off tests may be found in Kolstakis et al.[50]

3.3.2. Light-off test on engine bench

The light-off testing on an engine bench is better suited for the facilities of typical automotive laboratories. For this test the catalytic converter is mounted on the given exhaust system and the engine is braked to operate at a constant point. The converter is thus subjected to an exhaust flow of nearly constant flow rate and composition, whereas its temperature increases with time from ambient to a constant value. The conversion efficiency of the catalyst can be calculated based on inlet–outlet species concentrations as a function of inlet gas temperature. As before, the engine should be controlled to produce lean, rich and modulated A/F exhaust gas mixture.

A particularity of this test compared to the corresponding laboratory light-off test on a mini-scale sample is the temperature evolution at the catalyst inlet, which is principally dictated by the engine and exhaust piping transient characteristics (thermal response). Figure 6 presents the temperature evolution at the converter inlet and the conversion efficiency for CO and HC as functions of the inlet temperature measured in a full-scale light-off test.[39] The temperature increase rate is relatively steep and not sufficient to achieve uniform temperature distribution in the converter during the test. In the full-scale light-off activity test the catalyst is subjected to a generally non-uniform flow at its entrance. This, together with the heat transfer effects from the monolith to ambient, results in non-uniform flow and temperature conditions inside the converter, which adds to the complexity of catalyst assessment.

3.3.3. Redox scan

This type of test is necessary to distinguish catalyst efficiency for engine operation at various air-to-fuel ratios. Useful information can be derived regarding the efficient A/F operating region of the catalyst
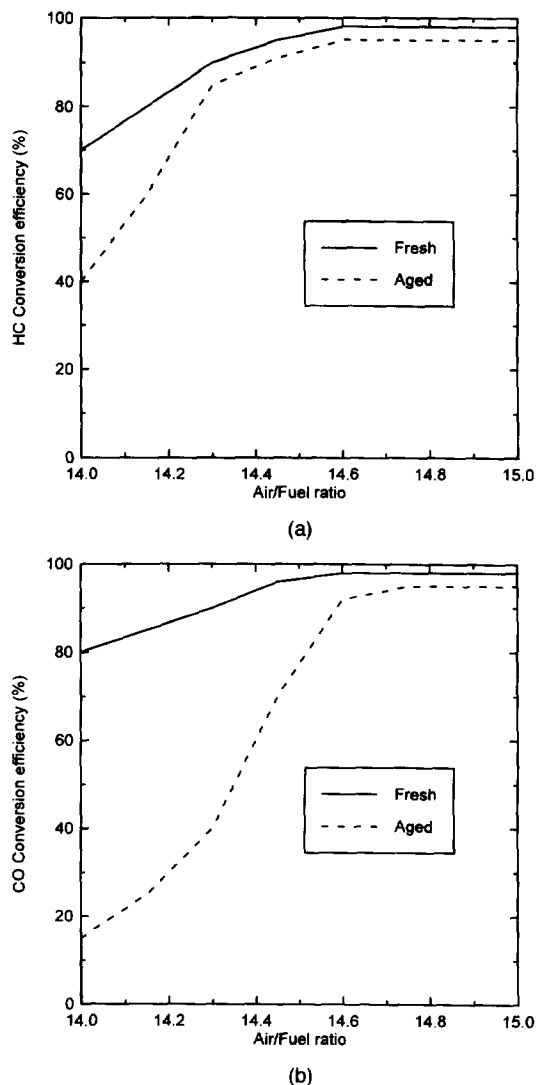
(a)

(b)

Fig. 7. Effect of 850°C fuel-cut ageing (5 h) on (a) HC and (b) CO performance of noble metal catalysts as function of A/F.[51]

(A/F window). This test can be performed either on a catalyst sample or on a full converter installed on a vehicle which can be externally controlled to operate at various A/F ratios. The redox scanning experiment can be performed for different exhaust-gas temperatures, which are safely above the light-off region, that is greater than 400°C.

As an example, we could invoke the experiment presented in Fig. 7.[51] This figure shows the HC and CO performances of fresh and aged (cycle A in Table 4) proprietary noble metal formulation three-way catalysts as a function of A/F ratio (A/F is varied between 14 and 15). High levels of conversion, rich of stoichiometric, are observed over the fresh catalyst. However, the aged catalyst shows a significant reduction of activity, which grows higher in the rich region. According to Summers and Silver,[51] mainly attributed to the loss of catalyst selectivity to the steam-reforming reaction.

For a more detailed analysis of the behavior of the catalyst as function of redox, it must be taken into account that certain differences occur depending on the direction of redox change. Specifically, the conversion efficiency observed during a lean to rich transition may differ from that observed during a rich to lean transition. An example of this behavior is described in Subramanian et al.[52] for methane conversion on Pd containing catalysts.

3.3.4. Oxygen storage assessment tests

In our previous discussion, it has been supported that the oxygen storage activity of the catalytic converter is mainly attributed to the oxidizing and reducing functions of Ce oxides present in the washcoat. According to this assumption, the maximum expected oxygen storage capacity expected for a catalytic converter may be calculated as half the amount of Ce atoms per unit of catalyst volume. However, this calculation usually yields results that are much higher compared to the experimentally observed storage capacities under operating conditions.[47] This is explained by the fact that only the active fraction of the oxygen storage component (CeO_2) participates in the transient processes occurring in real-world conditions. The values of model parameters, used to describe the oxygen storage–release functions of the converter (oxygen storage capacity, storage–release rates), can be estimated in laboratory conditions by producing a step change of inlet gas composition.

This test is based on the measurement of exhaust-gas composition downstream of the converter after a step change in its composition at the catalyst inlet. The step change can be realized by rapidly turning the

Table 4. Mechanisms of three-way catalytic converter ageing[53]

| Chemical	Thermal	Fouling	Mechanical
Poisoning: irreversible adsorption or reaction on/with the surface	Sintering (redispersion) Alloying	Carbonaceous deposits (coking)	Thermal shock Attrition
Inhibition: competitive reversible adsorption of poison percusor(s)	Support changes Noble metal–base metal interactions		Mechanical breakage
Poison induced reconstructing of catalytic surfaces	Metal/metal oxide-support interactions		
Physical/chemical blockage of support pore structure	Oxidation (alloy segregation) Noble metal surface orientation Metal volatilization		
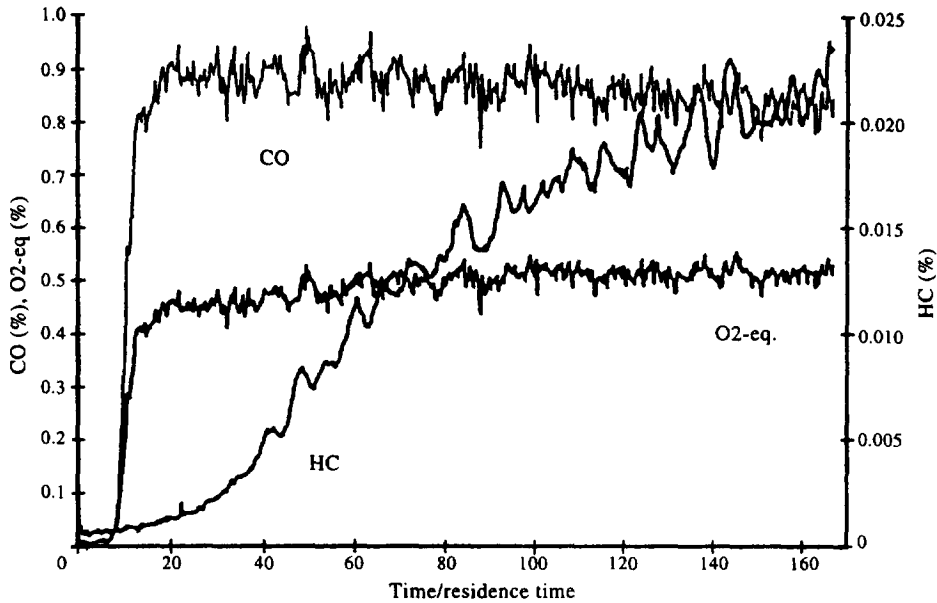
Fig. 8. Experimental results of a step change oxygen storage measurement. Step responses of HC, CO and O₂ equivalents after a step of 1% CO to the catalyst, which was operating at $\lambda = 1.01$ prior to the step. The space velocity was 30,000/hr and the temperature was 773 K.[47]
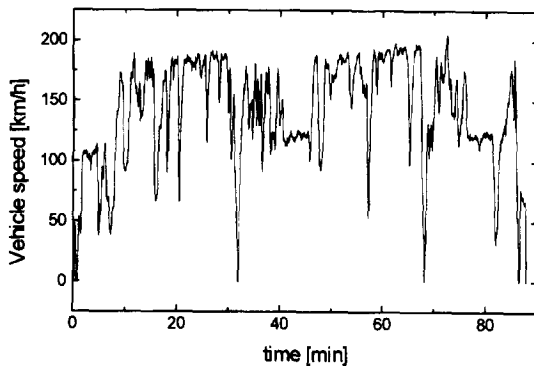

Fig. 9. Driving pattern of a typical European road ageing module representing highway driving conditions.[61]

mixture from lean to rich, by injecting a quantity of a reducing agent (e.g. CO). With the help of simple mass balance calculations the oxygen storage capacity and the associated rate parameters can be estimated. However, employment of this technique requires fast-response exhaust gas analyzers (diode-laser for the measurement of CO and flame ionization detectors for hydrocarbons).

Figure 8 presents experimental results regarding the CO and HC responses after a step change in inlet gas composition. By conducting such an experiment, we can calculate the oxygen storage capacity by using the following transient mass balance relationship:

$$OSC = \frac{\dot{N}}{V_{cat}} \int_{t_0}^{t_1} \left[\tfrac{1}{2}(CO)_{ss} - CO(t) \right.$$

$$\left. + \tfrac{9}{2}[(C_3H_6)_{ss} - C_3H_6(t)] \right] dt, \qquad (6)$$

assuming that the hydrocarbons of the exhaust gas are represented by propylene.

The assessment of the oxygen storage activity, by producing a step change in exhaust-gas inlet concentration and measuring the response of the exhaust gas exiting the converter, may also be employed in full-scale converters. In this case the step change may be produced by externally controlling the engine fuel control. The assessment methodology is identical to the one described in the previous section for laboratory environments.

An alternative method to test the oxygen storage activity of the converter is based on engine operation at modulated A/F ratio. The engine is externally caused to operate at a continually varying A/F ratio which is modulated between two values (lean–rich) with a relatively low frequency (e.g. 0.1 Hz). The load and speed of the engine are kept nearly constant, so as to ensure stable exhaust gas flow rate and temperature. The time averaged exhaust gas composition is measured before and after the catalytic converter. This test can be performed using conventional exhaust gas analyzers with no special response characteristics, provided the modulation frequency is sufficiently low.

3.4. Catalyst Deactivation—Ageing

3.4.1. Catalyst ageing mechanisms

Deactivation of automotive catalysts can result from various processes summarized in Table 4.[53] For current catalytic converter systems, deactivation during normal vehicle operation typically results from chemical and thermal mechanisms, rather than fouling and mechanical factors.

Prolonged catalyst exposure to high temperatures (above 850°C) is known to enhance reduction of the

Table 5. Typical fast ageing procedures used by various catalyst manufacturers (lean spike type)

Cycle	Mode	Mode duration [sec]	Inlet temp. [°C]	Bed temp. [°C]	λ	GHSV [/hr]	Total duration [hr]	Reference
A	1	60	850	905	1	68,000	100	Summers et al.[60]
	2	5	800	912	1.65	59,000		
B	1	60	760	825	1	72,000	100	Summers et al.[60]
	2	5	704	850	1.65	59,000		
C	1	100	880	925	1	92,000	100	Summers et al.[60]
	2	10	850	925	1.18	109,000		
D	1	180	900	N/A	0.98	75,000	60	Barley et al.[59]
	2	10	820	N/A	>4.5	5000		
E	1	50	805	860	1	N/A	100	Harkonen et al.[10]
	2	10	925	1000	N/A	N/A		
F	1	50	800	875	1	N/A	100	Harkonen et al.[10]
	2	10	890	930	N/A	N/A		

alumina surface area and sintering of the noble metals, resulting in losses of effective catalytic area. The dispersion of some important promoters/stabilizers, such as Ce, is also affected, which results in decrease of activity and oxygen storage capacity.[47] Surface loss of cerium in high temperature, oxygen-rich atmospheres can be retarded by the use of stabilizers such as La, Nd or Y. After high temperature oxidations, the use of stabilized cerias results in poor three-way activity, due to significant enrichment of the stabilized ceria surface with lanthana or neoydmia. The resulting activity loss can be partially reversed by reduction in H_2.[54] The most damaging scenario for the catalyst is its exposure to temperatures higher than 850°C in an oxidizing atmosphere (e.g. sudden braking after full load running of the vehicle).[55] Sustained engine misfiring caused by defects on the ignition module may also lead to severe thermal damage of the catalytic converter.[56]

The major chemical damages (poisoning) are caused by lead and sulfur contained in the fuel, as well as by oil additives such as zinc and phosphorous. Detailed studies about poisoning and thermal ageing mechanisms are available in the related literature.[2,57]

3.4.2. Accelerated catalyst ageing

A large number of ageing cycles have been developed by the catalyst and the vehicle manufacturers for accelerated testing of catalyst durability.[58-60] They fall into three broad categories, which are briefly presented below:

- vehicle ageing cycles;
- engine bench ageing;
- laboratory oven ageing.

A vehicle ageing cycle is supposed to represent, in the best possible way, the most severe real world driving conditions to which a given vehicle could be subjected during a typical catalyst lifetime (80,000–100,000 km). As an example Fig. 9 presents a road

testing module that is used by certain European automotive manufacturers as a part of a converter durability test procedure in prototype models. Analogous cycles are used by U.S. manufacturers (i.e. AMA durability driving cycle etc.). The use of such vehicle ageing procedures is normally limited to prototype testing due to the high associated cost.

A successful engine bench ageing cycle should comprise subjection of the catalyst to thermal loading, high temperature oxidation and presence of catalyst poisons. This tendency is also revealed by a study of existing accelerated ageing cycles of the lean spike type (Table 5).

As mentioned above, the major damage for the catalyst results from exposure to oxidizing atmosphere under high temperature. Such conditions are normally encountered during vehicle braking with fuel cut after running at moderate or high power. During this phase the temperature of the gas exiting the cylinders drops rapidly, since no fuel is burnt. The temperature of the gas entering the converter drops more slowly, due to the thermal inertia of the exhaust system. The fuel-cut is, however, accompanied with an instantaneous increase of hydrocarbons and CO emissions, resulting from incomplete combustion phenomena in the cylinders during the transient operating mode. Figure 10 shows the evolution of temperature, CO and HC concentrations of the exhaust gas entering the converter during a braking scenario with fuel cut, as measured on a 2000 cc car in the extra-urban part of the legislated ECE-EU cycle. The effect of the fuel-cut on catalyst temperature is investigated below, with the aid of a computer model for the prediction of transient catalyst behavior.[61]

Figure 10 (upper diagram) compares the catalyst temperature 50 mm from inlet for the cases of braking with and without fuel-cut. According to the simulation results, it is expected that, for the specific scenario, the catalyst temperature is about 50°C higher in the case of fuel-cut for a duration of 5–10 sec. This is due to the larger amount of
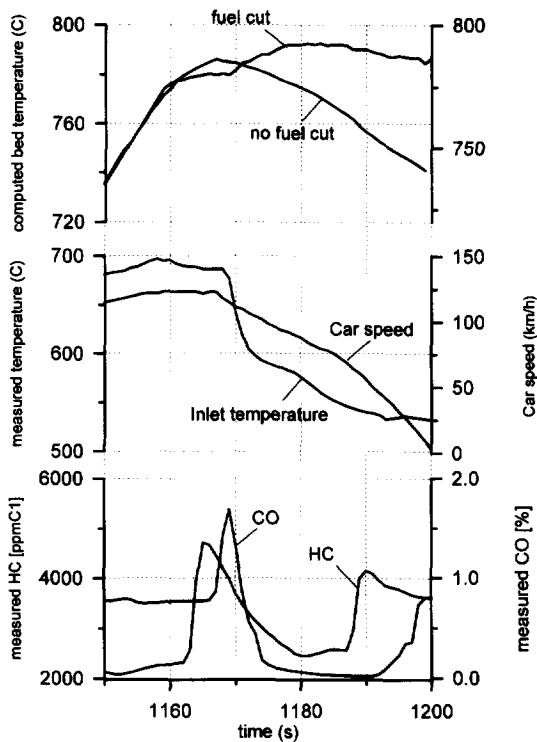
Fig. 10. Evolution of temperature, CO, HC concentrations of the exhaust gas entering the converter during a braking scenario with fuel cut, as measured on a 2000 cc car in the extra-urban part of the legislated European cycle. Comparison of computed catalyst bed temperatures with and without fuel cut.[61]

Table 6. Typical oven ageing procedures

	Gas feed	Temperature	Duration
1	1.5% CO, 0.15% HC, 0.1% NO, 20 ppm SO_2, 1.19% O_2	900°C	4 hr
2	N_2 + 10% H_2O	1200°C	3 hr
3	Air	980°C	95 hr
4	0.20% O_2 + N_2	1000°C	5 hr

combustible species entering the converter during the fuel-cut deceleration. The increased thermal loading under oxidizing atmosphere, produced in this case, dramatically increase the severity of the ageing conditions for the catalyst.

Table 6 presents some typical laboratory ageing procedures, which simulate high temperature oxidation and sintering of the washcoat and noble metals in an artificial atmosphere. In order to simulate severe ageing conditions in minimum time, the oven ageing is usually performed at very high temperatures, that are very rarely met in usual real driving conditions. Also, there are laboratory ageing procedures involving cycled feedstreams or using a pulse flame combustor.[62]

3.5. Catalyst Fast Light-off Techniques (FLTs)

3.5.1. General

Cold start HC and CO emissions contribute the majority of the total emissions in the legislated driving cycles. Figure 11 presents the cumulative CO, HC and NO_x emissions recorded in the European driving cycle for a gasoline vehicle. In order to minimize cold start emissions, special techniques have been developed and presented in the literature, referred to

as fast light-off techniques (FLTs). A review of existing FLTs shows that they may be categorized as follows:

(i) passive systems, employing exhaust system design changes (positioning of the catalytic converter closer to the engine, use of pre-catalysts or HC traps) in order to reduce cold start emissions;

(ii) active systems, which rely on the controlled supply of additional energy to raise exhaust gas temperature during cold start (electrically heated catalyst, burner, exhaust gas ignition with secondary air injection).

The main FLTs appearing in the literature are schematically presented in Fig. 12. A brief description of these systems is given in the following subsections.

3.5.2. Close-coupled main catalyst

Positioning of the catalytic converter closer to the exhaust manifold is an efficient way of increasing the catalyst inlet temperature levels during engine cold start. On the other hand, the resulting higher thermal loading under high-load engine operation may substantially accelerate catalyst ageing.

Recent developments in catalytic washcoating technology have led to the production of highly stable Pd-containing catalysts, even at temperatures as high as 1000°C.[63] Since Pd is also effective regarding the HC light-off behavior hydrocarbons, it has proven appropriate for use in close coupled catalysts.

It seems that converter close coupling is an effective means for reducing cold start emissions, as long as the converter remains reasonably active. In order to comply with the legislation regulations regarding converter useful life, great care should be placed on the selection and design of a close coupled catalyst.

3.5.3. Pre-catalyst

In this technique the main catalyst remains at its initial position, whereas the pre-catalyst is usually placed in the vicinity of the exhaust manifold. Pre-catalysts should be carefully designed regarding their formulation and volume. The pre-catalyst volume is usually small (10–30% of the main converter
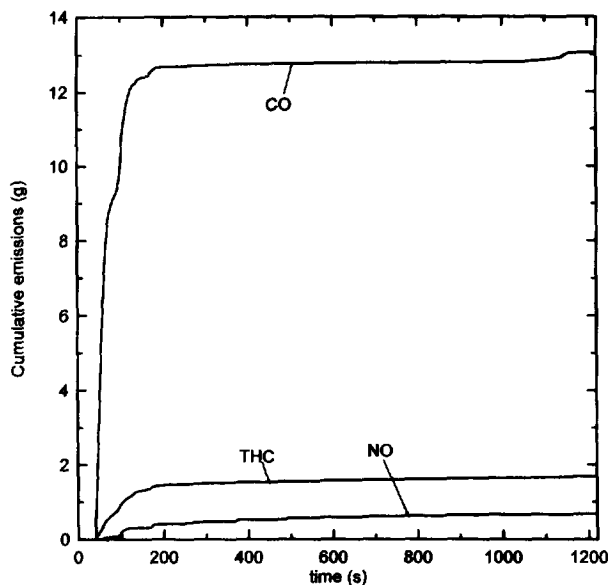
Fig. 11. Cumulative CO, HC, NO$_x$ emissions of a 2 l gasoline car in the new European driving centre.

volume), in order to allow installation close to the exhaust manifold without any required modification to the car underfloor. Larger pre-catalysts exhibit a higher thermal inertia, resulting in slower warming-up of the main converter. Usually, an optimum pre-catalyst volume in terms of overall efficiency and cost can be determined with computer aided engineering.[64]

The common formulation for precatalysts is either Pd–Rh or Pd-only with high precious metal loading (usually three times the loading of the main converter, i.e. in the range of 150 g/ft^3), thus favoring exothermic oxidation reactions and consequently producing heat utilized to heat-up the main catalyst brick.

3.5.4. Hydrocarbon adsorber systems

Another approach to cold-start hydrocarbon emissions control is related to the use of hydrocarbon adsorber systems (also referred to as hydrocarbon traps). The material employed to adsorb hydrocarbons at temperatures below 200°C is constantly being improved, from the initial activated carbon to special zeolite adsorbers.

Figure 13 (a) shows a hydrocarbon adsorber system combining a start catalyst with a heat exchanger composed of two 3WCC beds and a hydrocarbon trap.[65] During the cold start, the exhaust gas flows unconverted through the start catalyst and the first pass of the catalysed heat exchanger and on into the hydrocarbon adsorber, where HC is removed via physisorption. The first 3WCC bed is, thus, cooled by thermal contact with the second bed, which is located far downstream. On the other hand, during the critical phase of HC desorption from trap, the second bed has been already warmed up by the first bed, thus reaching light-off in time to oxidize the

desorbed hydrocarbons. Naturally, a high HC conversion efficiency during the desorption phase requires additional air injection.

A more recent development in HC adsorber systems, avoiding the complexities of a heat exchanger between 3WCC beds, is shown in Fig. 13 (b).[66] The vacuum actuated main diversion valve (V1) is readily closed completely, to pass the exhaust gas over the adsorbers, or opened to allow the exhaust gas to pass directly through the main exhaust pipe line. In order to regenerate the adsorbers with the hot exhaust gas it is necessary to heat the adsorbers while not allowing the second catalyst to drop below its light-off temperature. Should the second catalyst temperature drop too much it would allow the desorbed HCs to be emitted through the tail-pipe. The fractional opening of the vacuum actuated valve is varied and controlled by bleeding air into the vacuum line through a needle valve.

To avoid the complexities of by-passing the HC adsorber, in-line HC adsorber systems are studied and tested in various versions.[67,68] An advanced system employing a fluidics diverter valve is shown in Fig. 13 (c). The system consists of a first catalyst followed by an adsorber unit with a central hole and a downstream second catalyst. During cold start, the exhaust gas passes through the adsorber substrate channels and the central hole. The hydrocarbons are adsorbed from the exhaust gas passing through the channels and a portion of the exhaust gas passing through the hole impinges directly on and heats the second catalyst. A fluidics diverter is used to divert the exhaust gas through the adsorber unit and away from the central hole during cold start. After the fluidics diverter is turned off most of the exhaust gas flows directly through the hole to the second catalyst, thus
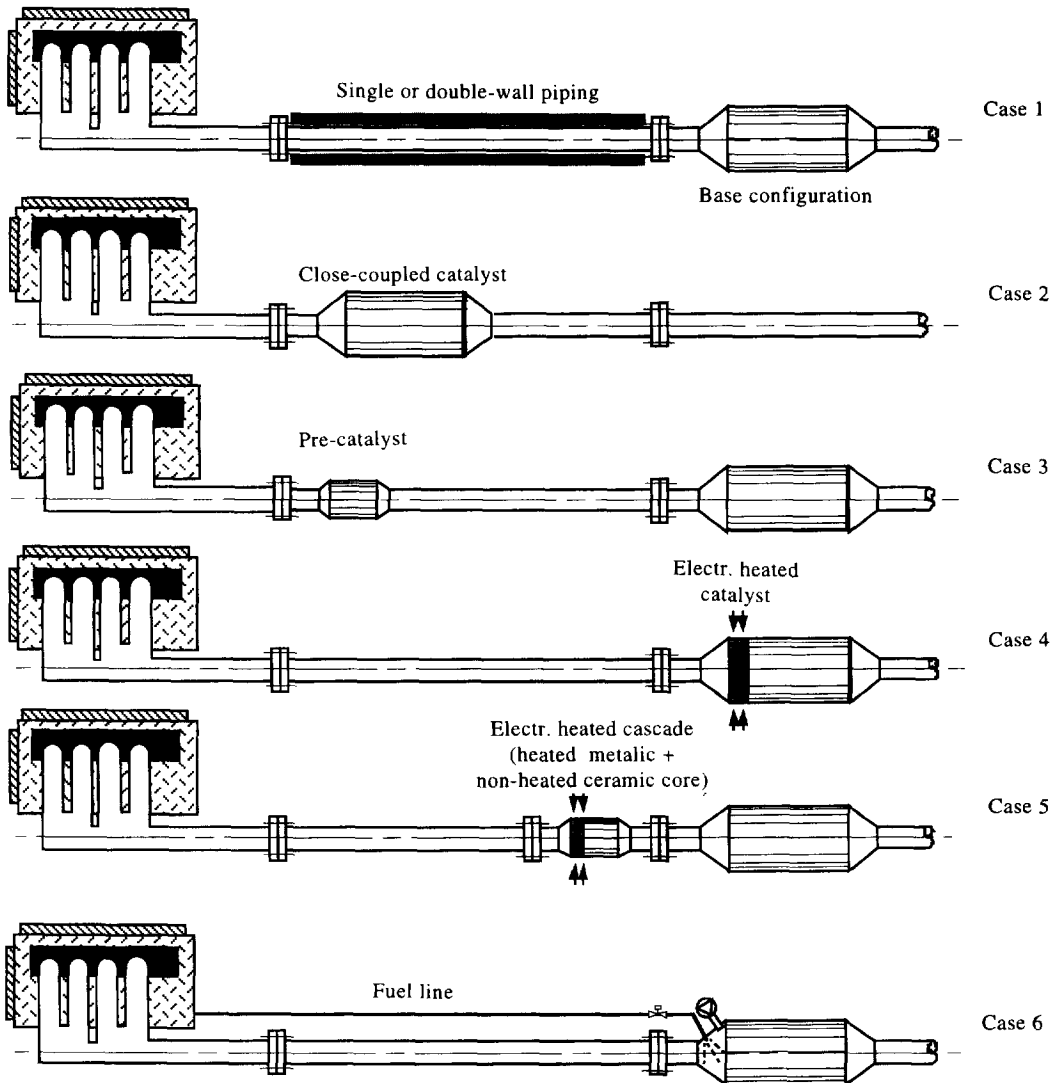
Fig. 12. Schematic of the main fast light-off techniques.

heating it faster than the adsorber unit. As the adsorber is heated the HCs are slowly desorbed and oxidized over the second catalyst.

Based on the most recent developments, HC trap technology could present a viable alternative to fast light-off techniques regarding HC emissions reduction capability (reported total HC emissions 45–75% relative to standard 3WCC system). Further work is needed to develop simple (passive), durable HC trap systems with HC desorption temperature higher than typical catalyst light-off temperatures.

3.5.5. Electrically heated catalyst (EHC)

The demands posed by the on-coming ULEV standard can be successfully met with the use of an electrically heated (pre)catalyst (abbr.: EHC)[69,70] as an addition to the main catalytic converter. The low mass EHC quickly reaches high temperature levels,

sufficient for a limited CO and HC conversion. The heat generated by the exothermic oxidations is carried down by the exhaust gas to the main converter, which consequently attains faster light-off.

It has been reported[69,70] that this technique could be optimized if the following measures are taken:
- positioning of the heated precatalyst close to the main catalyst brick;
- positioning of the heated pre-catalyst and the main catalyst close to the engine (i.e. exhaust manifold);
- reduction of the heated pre-catalyst mass;
- beginning of heat supply (8–10 sec) before the engine start.

Moreover, it is claimed that the most effective scenario consists of a combination of pre- and post-crank heating.[71] This is due to the fact that when the heating begins a few seconds before engine crank, the total amount of the provided power is consumed for increasing the temperature of the metallic catalyst
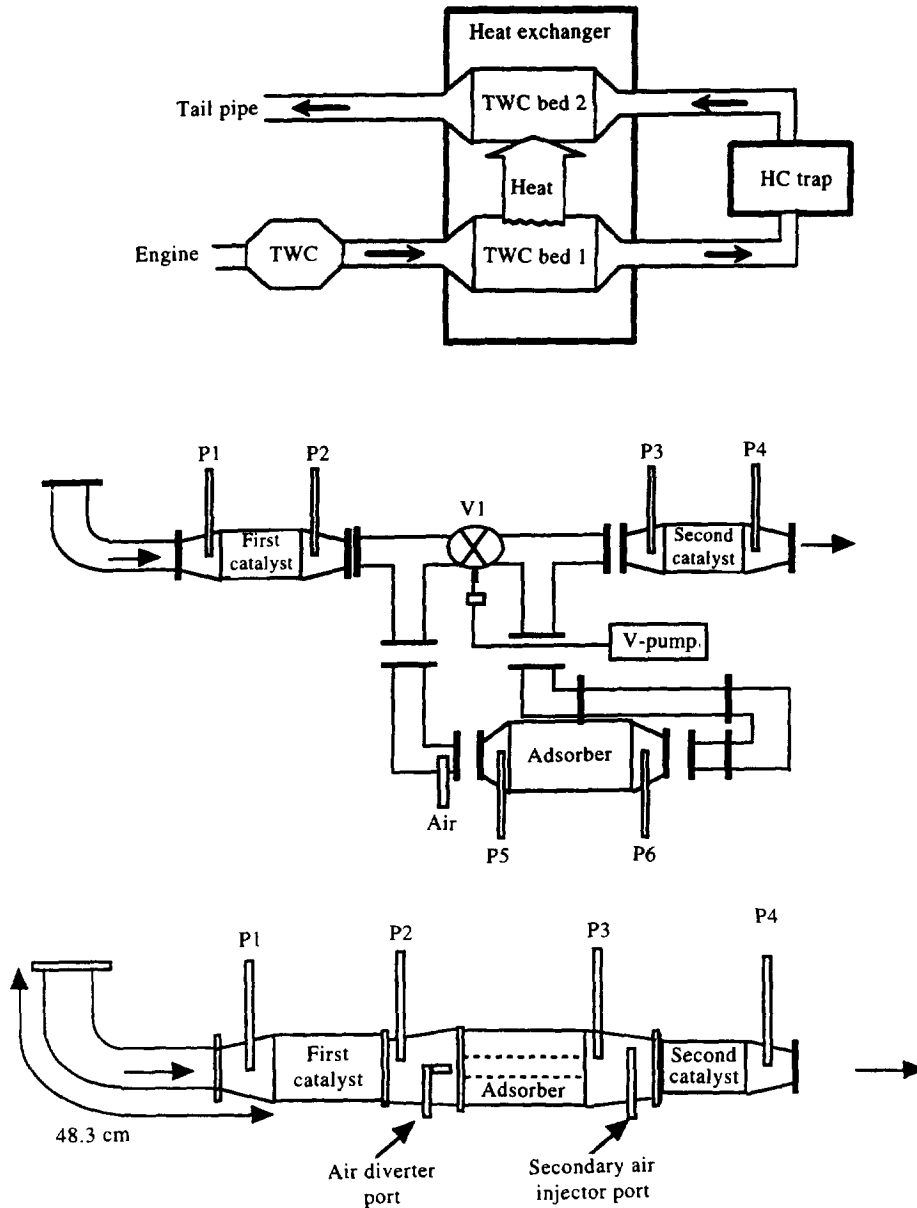
Fig. 13. Schematic of hydrocarbon trap systems.

substrate. When the engine is started through, the substrate must have already reached a high temperature (more than 250°C), so that reaction exotherm compensates for the cooling effect caused by the exhaust gas flow. A short pre-crank heating has been suggested, although this is not a practical solution.

However, a full-featured EHC system can be rather complex, as well as expensive. The EHC is electrically connected with the vehicle electrical system, including an electronic power switch, the purpose of which is to actuate the heating current, to monitor the whole system and allow for the exchange of necessary data with the engine management system. Also provided are additional diagnostic lines, which measure the EHC voltage. The heating current can be alternatively supplied by either the vehicle battery, an additional battery, the alternator or a high-power capacitor. The heating scenario is provided by the engine management system, which also controls the whole procedure. A current of secondary air, supplied during the heat-up phase can improve the efficiency of the system. The air supply is also controlled by the engine management system.

Significant improvements in the cold start HC emissions may be attained by the employment of an additional mini catalyst between the EHC and the main converter. This is referred to as 'cascade system' in the literature.[70,72] Figure 14 presents the significant improvements attainable with such systems, which
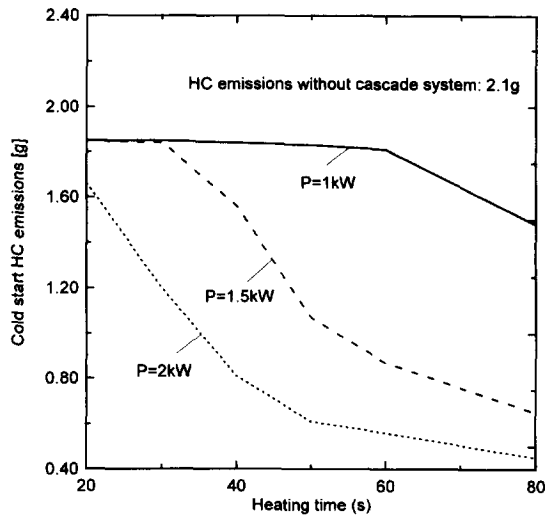
Fig. 14. Reductions in HC emissions achieved with a cascade
EHC system for different heating powers.

implies that the mini converter assists in a better
exploitation of the external energy supply.

The effectiveness of the electrical heating concept is
sensitive to the engine operation during the first
minute from start. A rational optimization should
additionally comprise feedback control of the power
supply timing based on signals from temperature or
HC sensors.[73]

On-board diagnostics requirements of such systems
are also demanding and add to the system complexity.
Detected system errors must be stored by the engine
management system and be able to be extracted by a
diagnostic tester.

3.5.6. Fuel burner

The use of a burner system is a straightforward way
to heat up the catalyst. Figure 12(f) is a simplified
schematic of a burner catalyst system. The combus-
tion chamber is located just in front of the converter
to ensure rapid and efficient heat transfer. When the
engine is started a temperature sensor, located on the
converter shell, checks whether the catalytic converter
is above or below its light-off temperature.[74] If it
detects a lower temperature, the burner is turned on
for a certain period of time defined by the temperature
level. With the start of the burner the secondary air
pump and ignition are switched on and shut-off valves
for both fuel and secondary air are opened. By
means of a sparking voltage the primary side of the
ignition module detects whether the ignition function
is working properly. Only when this condition is met,
the fuel is added by controlling the fuel supply system,
metered in the fuel regulator to a constant flow
rate and supplied to the burner nozzle virtually at
atmospheric pressure. As soon as a sufficiently high
catalyst bed temperature is sensed, both secondary air
and fuel supply shut-off values are reset to their
normally closed positions.

Burner systems are presented as alternatives to
EHC, claiming that the energy consumption asso-
ciated with their application is significantly lower.
This is true because of the poor efficiency of the
system 'engine plus alternator' in producing electrical
energy to be dissipated in the EHC resistance. On the
other hand, real world burner systems are of high
complexity, equipped with a number of control valves
and sensors, which are micro-processor controlled. A
significant part of the complexity and relatively high
cost associated with such systems is due to the need to
comply with safety regulations.

3.5.7. Exhaust gas ignition (EGI)

Exhaust gas ignition systems have been employed
in order to avoid added cost and complexities, as well
as safety concerns, associated with the gasoline
supply of the burner systems. For the employment
of EGI the engine operates initially with very rich
fuel conditions, allowing a combustible exhaust gas
mixture to reach the catalyst inlet where it is ignited
with the help of a spark plug, located at the converter
inlet.[75] An electric pump provides the additional air
required for the combustion of the exhaust gas
mixture. Only part of the fuel is burned in the
combustion chamber, whereas the remaining part
(main active species is H_2) is ignited at the catalyst
inlet face. The conditions necessary for a cold non-
reacting mixture of combustible exhaust gases to be
ignitable in the afterburner at ambient temperature
are examined in Collins and Hands.[75]

3.5.8. Secondary air–rich fuel mixture

During the cold start phase, most engines must be
run with richer than stoichiometric fuel mixtures, in
order to ensure smooth operation without stalling.[76]
The consequent lack of oxygen in the catalytic
converter allows for only partial oxidation of CO
and HC, thus resulting to higher exhaust gas
emissions. This problem is handled by injecting a
secondary current of air after the exhaust valves of the
engine.

Secondary air injection requires a separate piping
system, as well as an electrically driven air pump,
which blows the additional air into the exhaust
manifold, just after the exhaust valves.

The injected air can react with the hot exhaust gas,
thus allowing for an initial oxidation of CO and HC
to take place in the exhaust piping. The heat produced
by the oxidation reactions increase the exhaust gas
temperatures, resulting in a fast catalyst light-off. The
light-off time achieved with this system in FTP-75 test
cycle is less than 40 sec (compared to 100 sec of the
conventional catalytic system).[76] The respective
reduction of cumulative HC emissions in the FTP-
75 test can reach even 50% (depending on the engine
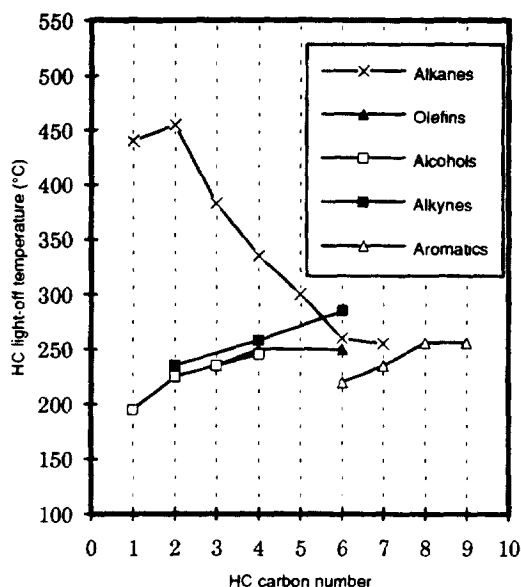and exhaust piping characteristics).

Fig. 15. The effect of hydrocarbon structure on its light-off temperature.[77]

Table 7. Malfunctioning criteria for catalytic converters for different emission technology vehicles

Legislation	HC	CO	NO$_x$
	Failure limit (g/km)		
EPA	0.12*	1.06*	0.31*
CARB (TLEV)			
CARB (LEV)	1.5 times the respective		
CARB (ULEV)	emission limits		
E.OBD	0.4	3.2	0.6

* Increase above emission limits.

3.6. Catalysts for Alternative Fuelled Engines

Methane is much more effective than carbon dioxide at absorbing infrared radiation: it has been estimated that each molecule of methane in the atmosphere has a greenhouse effect equivalent to 25 molecules of carbon dioxide. This fact has led to significant concern, especially in Europe, on the development of dedicated catalysts for exhaust aftertreatment of spark-ignition CNG engines.

Methane is a very stable molecule[77] and, thus, requires very high temperatures to be catalytically oxidized (Fig. 15). In order to reduce methane emissions during the first few minutes of operation after the start of the engine, the light-off temperature for methane has to be lowered. To reach this goal several precious metals were tested for their methane oxidation activity.[78–80] The results clearly indicated that Pd containing catalysts are the most active for the oxidation of methane, especially under slightly lean conditions. Furthermore, under real CNG engine exhaust conditions, i.e. high water vapor and low CO concentrations, Pd containing catalysts showed a significant higher stability as compared to standard Pt–Rh catalysts.[81]

Furthermore, the efficiency of the methane selective catalyst is highly sensitive on the A/F ratio of the exhaust gas. To overcome this problem, tighter and improved fuelling control is necessary in CNG fuelled engines.

Catalytic control of exhaust emissions for methanol or variable fuelled vehicles may present problems, because many catalysts have been shown to exhibit tendencies to partially oxidize unburned methanol to formaldehyde at temperatures typically encountered during the converter warm-up period.[82,83] Thus, the ideal exhaust catalyst for a methanol fuelled exhaust should possess additionally both high activity and high selectivity for the complete oxidation of methanol. The computational study presented in Oh and Bissett[84] indicates that the total amount of aldehyde emissions may be reduced by reducing the time needed for catalyst light-off.

3.7. On-board Diagnosis for Catalytic Converters

3.7.1. OBD system requirements

Modern studies on the vehicle related air pollution suggest that improved air quality standards could be achieved by monitoring and controlling the current technology vehicle emissions, instead of imposing new ultra-low compliance standards for new cars.[85] In this respect, improved inspection and maintenance programs, remote sensing and on-board diagnosis are expected to play an ever increasing role.

Since 1988 the State of California required all cars sold in California to be equipped with a first generation on-board diagnostics system (OBD I). Thus, after a 3-year phase-in, by 1990, all cars sold in California were equipped with some minimum OBD capability.[86] First generation OBDs did not monitor many important emission control subsystems, such as the evaporative emissions system, the secondary air injection and the catalytic converter.

Second generation (OBD II) systems, introduced since 1994, must cover the catalytic converter, the lambda sensor, engine misfiring and alert the operator of any possible malfunction or need for repair to emission control parts. *Analogous regulations are projected for Europe by 2000.* Table 7 summarizes the malfunctioning criteria for catalytic converters in North America (EPA), the state of California (CARB) and Europe (E.OBD).[87]

A diagnostic system for the catalytic converter installed on vehicles is expected to detect failure to achieve the required purification efficiency and, in this case, warn the car owner for the necessary system service. As it is both impractical and expensive to directly measure the conversion efficiency of a catalytic converter on-vehicle using exhaust gas analysis, integrated methodologies are necessary to indirectly assess catalyst performance by processing

Table 8. Overview of on-board catalyst diagnosis systems

|	On-board catalyst diagnosis					
Method	Dual lambda sensor		(Dual) HC sensor		Temperature sensor	
Sensors	HEGO	UEGO	Thick film	Surface ionization	Thermistor	Resistive
Diagnosis principle	Measurement of O_2 storage capacity		HC conversion		Detection of exothermic heat	
Suitable operation mode	Steady-state operation (hot engine)		All modes (hot engine)		Variable, also transient operation	
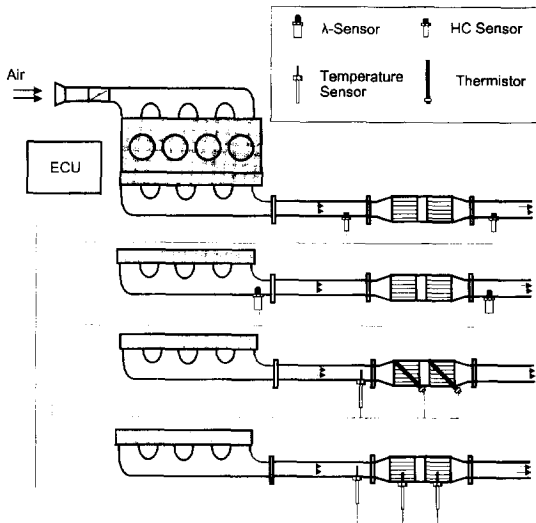
Fig. 16. Exhaust system configurations for different OBD systems.

of easy-to-measure quantities. It is highly desirable for such a methodology to combine:

- simplicity of measuring devices installation;
- relatively simple signal processing, low loading of the electronic control unit (ECU);
- low cost of additional equipment;
- high durability of OBD equipment;
- applicability to variable emission control systems configurations;
- applicability to transient real-world driving.

3.7.2. Catalyst monitoring techniques

In spite of the progress made so far, the development of reliable and cost-effective OBD systems remains problematic, especially for modern low-emitting vehicles.[88] Table 8 summarizes the main possible approaches for on-board catalyst diagnosis, which are briefly reviewed below. The exhaust system configurations for the different OBD system installed are schematically drawn in Fig. 16.

As a consequence of its oxygen storage components, a properly working catalyst would be able to dampen oxygen fluctuations in the exhaust stream, when the vehicle is operating under stabilized speed and load conditions.[89] On the other hand, a catalyst with reduced oxidation activity and oxygen storage

ability would allow more free oxygen to pass through unreacted, thus resulting in overall performance loss. The idea to install a second lambda sensor after the 3WCC has been proposed as a method to detect catalyst deterioration since 1978.[90] In the same monitoring philosophy belong the specially designed UEGO[91] and NEEGO[92] sensors, which present improved characteristics compared to the conventional HEGO sensor. The main practical problem associated with the use of lambda sensors as OBD devices is the difficulty in obtaining a sufficient correlation between the oxygen storage capacity and the overall converter efficiency in real driving.[93,94] Nevertheless, this technique is currently used to monitor catalytic converters for the state-of-the-art vehicles in U.S. In order to detect catalyst malfunctions in ULEV vehicles, the dual lambda sensor technique has not yet proven sufficient.[95]

Measurement of hydrocarbons in the exhaust gas is the most direct way to monitor catalyst efficiency. The feasibility of this technique, however, strongly depends on the development of HC sensors applicable to vehicles exhaust systems at a rational cost. Recently, two types of HC sensors have been presented in a preliminary stage, namely, the potentiometric solid electrolyte sensor[96] and the surface ionization detector.[97] Thick-film potentiometric sensors are not yet (1996) commercially available. Although very promising for on-board diagnosis and control for new technology vehicles, application of these sensors depends on the reduction of manufacturing cost. As regards the surface ionization sensors, their ability to detect differences in HC concentration before and after the catalytic converter as well as engine misfires has been demonstrated. However, significant work remains to be done in order to render the detector feasible for OBD purposes. This work concerns detector contamination, processing of very small currents, stability over long term operation and durability. The HC sensor installed in the exhaust system can simultaneously be used for purposes other than catalyst diagnosis. For example, in the case of an electrically heated catalyst system, the sensor signal can be used to control the electrical heating. Excessive energy supply can thus be avoided for properly working systems, whereas catalyst retarded light-off behavior due to ageing can be compensated for by prolonged heating.
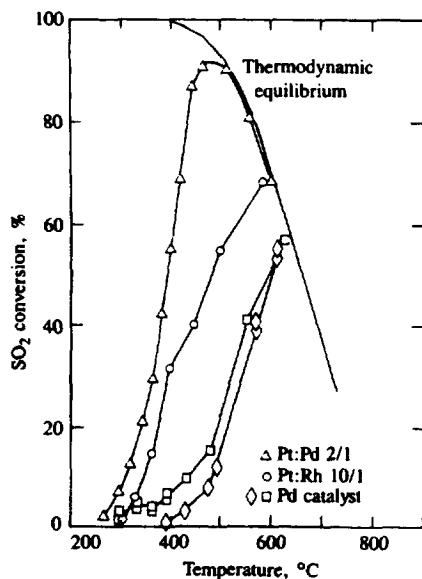
Fig. 17. SO_2 conversion to SO_3 as a function of temperature with 5% O_2 concentration and no reducing species present. Space velocity 10/sec. Results for Pt–Rh, Pt–Pd and Pd catalysts.

Exhaust gas temperature monitoring inside the catalytic converter can provide useful information about heat release caused by exothermal reactions, which is an indication of catalyst light-off.[98] Deactivation of the front catalyst part causes a shift of the main reaction zone in the direction of the flow, so that different temperature profiles along the substrate are expected during the course of ageing. Thus, a single temperature measurement in a fixed position would probably not be sufficient to monitor exothermal heat release over a long operating period.

A number of studies related to thermal methods for catalyst diagnosis have been recently presented. Collins et al.[99] proposed that a linear temperature sensor be installed diagonally in the catalyst bed. A linear sensor (made by high temperature thermistor material) can detect local over-temperature conditions anywhere along its length, by indicating a temperature that is much more dependent on the maximum temperatures encountered over its length than on the lower ones. The sensor signal may then be processed to indicate whether exothermal reactions, mainly CO and HC oxidation, take place in the catalytic converter or not. The computational studies of the above authors have shown that for practical engine/catalyst combinations the 'hot region' of the monolith lies in the order of 10–30 mm. The same studies have shown that using a sensor, which is about up to five times longer than the hot region, the indicated temperature approximates the real maximum temperature with sufficient accuracy. Linear temperature sensors become more attractive if they are used simultaneously for monitoring other emission control functions (exhaust gas ignition, catalyst temperature management) or detection of engine misfire.

The main problem with the temperature measurement techniques remains the definition of a universally valid monitoring method, principally applicable during each driving scenario. One such method applicable to metallic substrate converters is proposed in Pelters et al.[100] During the deceleration fuel cut-off phase the temperature difference between the metal catalyst substrate and the exhaust gas entering the converter is obtained. The substrate temperature measurement involves resistance sensors specially integrated between the layers of the metallic foils. Due to the very small temperature differences during a fuel cut-off phase, it is necessary to intensify the signals, so as to enable a clearer distinction between the fresh and the aged converter. To this end, a predefined quantity of fuel can be injected with the help of the fuel injection system with turned off ignition. The temperature signals obtained can be electronically processed by differentiation, to distinguish between a working and a defective catalyst. Research in this field is currently carried out in order to assess applicability of such techniques for large scale utilization.

Methods based on energy balance calculations to assess the exothermic heat generated during random engine operation have shown initially promising results.[101,102] Suitably developed algorithms are used to calculate the energy released per unit mass of exhaust gas flowing through the converter. This value correlates sufficiently with overall catalyst efficiency. To employ this method for a pre-catalyst, two temperature sensors are sufficient. For larger volume main catalysts, a third sensor may be necessary. These techniques could probably support OBD for ultra low emitting cars, equipped with 'fast light-off' systems, including pre-catalysts or electrically heated catalysts.

3.8. Mathematical Modeling of 3WCC

3.8.1. Historical review

Mathematical modelling of monolithic catalytic converters has been employed over the last 25 years to assist the design and development of automotive exhaust aftertreatment systems. Kuo et al.[103] developed a lumped parameter model for the monolithic converter, which has been used by a number of automobile and oil companies. Vortruba et al.[104] have also presented a similar model. Young and Finlayson,[105] in a pioneering work, have developed and solved a two-dimensional channel model for a monolith using orthogonal collocation. They discussed in detail the applicability of the quasistatic assumption for the gas phase for transient cases. Heck et al.[106] showed that a simpler one-dimensional model is adequate for predicting monolith behavior. They also presented analytical solutions for the adiabatic temperature under steady state operation. Lee and Aris[24] reported a two-dimensional model that also included heat radiation effects. Otto and LeGray[107]

validated their model with experimental results and presented model predictions regarding converter efficiency for different exhaust system designs. Their model also included radial conduction effects in the monolith. Oh et al.[108] presented a model for the pellet type catalyst. Extensive verification of this model by engine bench experiments is given in Oh and Cavendish.[109] This model was employed for the prediction and parametric analysis of vehicle exhaust emissions during warm-up.[110]

Most of the above mentioned modeling studies were focused on the behavior of adiabatic monoliths exposed to a uniform flow distribution at the front face. In this case, temperature and concentration profiles in all channels of the monolith are the same, so that consideration of only one channel would be sufficient. However, actual automobile converters operate in a nonadiabatic mode, under conditions where the gas flow is distributed non-uniformly at the monolith inlet. Flytzani-Stephanopoulos et al.[111] dealt with the two-dimensional (axisymmetric) heat transfer process in a non-reactive monolith. Becker and Zygourakis[112] presented two-dimensional solutions for an adiabatic reacting monolith, using a simplistic reaction scheme considering only CO oxidation and neglecting the effects of heat transfer through the surrounding materials. Chen et al.[113] developed a comprehensive three-dimensional model for the analysis of transient thermal and conversion characteristics of monolithic catalytic converters.

All of the above mentioned models relied on the historical data provided by Voltz et al.[36] which refer to CO and HC oxidation in a lean environment on a platinum catalyst. The rate expressions are of the Langmuir–Hinshelwood type and account for the inhibition due to CO, HC and NO. This approach was sufficient for modeling oxidizing catalytic converters. However, three-way catalytic converter modeling should account for the reaction mechanisms in operating conditions very close to stoichiometry, which pose additional challenges.

Gottberg et al.[114] presented a detailed channel model, which took into account independent adsorption from gas phase to surface site, surface reactions ('electron transfer') and desorption from surface to gas phase for the following five chemical species: CO, CO_2, O_2, NO and C_3H_8. The authors conducted extensive trial simulation work aiming at achieving a satisfactory model validation against real emission data under different dynamic conditions, using minor (empirical) adjustments of adsorption, desorption and reaction rate constants. Montreuil et al.[38] presented a concerted effort aiming at the compilation of an experimental database of steady-state catalyst conversion efficiency for two catalyst formulations, for the purpose of updating the kinetic rate constants in the Ford 3WCC model.[107] They employed an extended reaction scheme comprising 13 reactions and derived redox dependent kinetic expressions, which are valid above 371°C.

Pattas et al.[39] presented a transient 1-D modeling approach for the 3WCC embodying an oxygen storage and release submodel. The model relied on a simplified five reaction scheme comprising CO, H_2 and HC oxidation and NO reduction by CO. A similar approach for the reaction scheme, lacking oxygen storage, was presented in Siemund et al.[115] A two-dimensional model with an extended reaction scheme and a more comprehensive oxygen storage submodel is presented in Kolstakis et al.,[49] along with an investigation of the model application extents in common automotive applications. This category of models are routinely used by auto-manufacturers for design optimization of exhaust aftertreatment systems based on 3WCCs.

The main problem in the evolution of this category of transient 3WCC models is the lack of adequate kinetics data covering a significant number of reactions, for the multitude of catalyst formulations and washcoats employed in automotive applications. Moreover, the situation is further complicated by the effect of various modes and degrees of catalyst ageing during vehicle operation. For this reason, it has become common practice to rely on tunable kinetics expressions, which should supply a satisfactory number of degrees of freedom for the model.

3.8.2. Governing equations for the reactor model

As mentioned above, two main directions in the modeling of the transport processes in the monolithic channels have appeared in the related literature: simultaneous 3-D solution of the energy and mass balance equations of the boundary layer has been presented in Young and Finlayson[105] and Spicher and Lepperhoff.[116] The simplified approach of employing the well-known Nu and Sh functions for the flow in closed ducts has been followed in the great majority of the 3WCC models presented. The latter approach offers simplified, less time-demanding 1-D handling and practically equivalent accuracy levels. In the following, the main assumptions and the governing differential equations used in mathematical models of monolithic catalytic converters will be briefly presented.

Most of the recent advanced three way converter models feature:

1. Computation of the convective heat and mass transfer from the exhaust gas to the catalytic surface. A 'film approach' is adopted, employing mean bulk values for the gas phase and solid–gas interface values for the solid phase species concentrations. The corresponding transfer coefficients are computed using spatial dependent relations for Nusselt and Sherwood numbers, applicable to laminar flows in ducts.
2. Computation of the heterogeneous chemical reactions taking place on the catalytic surface based on Langmuir–Hinshelwood based rate

expressions. 'Lumping' of surface adsorption–desorption and pore diffusion phenomena in the kinetic rate expressions. Neglection of the contribution of homogeneous reactions, since their reaction rates are important only at unusually high temperatures.

3. The 3-D transient temperature field in the converter is computed, taking into account the heat conduction in the substrate and the surrounding insulation, and the heat losses to the surroundings via convection and radiation. The contributions of the convective heat transfer in the channels and the exothermal heat release are taken into account by respective source terms.

4. The oxygen storage and release phenomena in the washcoat are described by the dynamic redox activity of the cerium oxides present in the catalytic layer. Tunable kinetic rate expressions are employed to represent catalyst performance in a wide range of temperature and redox environments.

The transient behavior of the catalytic converter is computed as a series of quasi steady-states. The differential equations describing the conservation of mass and energy in the catalytic converter are given below:

mass balance in the gas phase

$$w \frac{\partial c_{g,i}}{\partial z} = -\rho_g k_i S(c_{g,i} - c_{s,i}); \tag{7}$$

energy balance in the gas phase:

$$w C_{p,g} \frac{\partial T_g}{\partial z} = hS(T_s - T_g); \tag{8}$$

mass balance in the gas–solid intermediate phase

$$\left(\frac{M_g}{\rho_g}\right) R_i = k_i S(c_{g,i} - c_{s,i}); \tag{9}$$

energy balance in the solid phase

$$(1 - \epsilon)\rho_s \frac{\partial (C_s T_s)}{\partial t}$$
$$= (1 - \epsilon)\left(\lambda_x \frac{\partial^2 T_s}{\partial x^2} + \lambda_y \frac{\partial^2 T_s}{\partial y^2} + \lambda_z \frac{\partial^2 T_s}{\partial z^2}\right)$$
$$+ hS(T_g - T_s) + \sum (-\Delta H)_j R_j. \tag{10}$$

Based on the theoretical ground of the Langmuir–Hinshelwood theory, the reaction rates are usually expressed in the following form:[36]

$$R = \frac{A \, e^{-E_1/RT} c_{CO} c_{O_2}}{G}. \tag{11}$$

The variable G represents an inhibition factor of the form

$$G_1 = T(1 + K_1 c_{CO} + K_2 c_{C_3H_6})^2$$
$$\times (1 + K_3 c_{CO}^2 c_{C_3H_6}^2)(1 + K_4 c_{NO}^{0.7}). \tag{12}$$

Similar expressions are used for the other reactions.

Details on kinetic rate expressions and constants used in 3WCC modeling can be found in the related references.[36–40,49,56]

According to Koltsakis et al.[49] and Herz,[117] the oxygen storage mechanism may be described by the oxidation and reduction of the Ce oxides present in the washcoat according to the following reaction:

$$2CeO_2 \rightleftarrows Ce_2O_3 + \tfrac{1}{2}O_2. \tag{13}$$
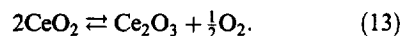
The reaction to the right denotes the release of an oxygen atom, which is made available to react with a reducing species of the exhaust gas (e.g. CO). The left direction of the reaction represents the storage of an oxygen atom by increasing the oxidation state of Ce_2O_3. In order to express the fractional extent of oxidation of the oxygen storage component, the auxiliary number ϕ may be defined as:

$$\psi = \frac{2 \times \text{moles CeO}_2}{2 \times \text{moles CeO}_2 + \text{moles Ce}_2O_3}. \tag{14}$$

Oxidation rate is considered proportional to the oxygen storage capacity (OSC), to the local oxygen concentration as well as to the difference $1 - \psi$; analogously, the reduction rate should be proportional to ψ and dependent on the local CO concentration:

$$R_{ox} = k_{ox}[O_2]OSC(1 - \psi) \, \text{mol/m}^3/\text{sec}, \tag{15}$$

$$R_{red} = k_{red}[CO]OSC\psi \, \text{mol/m}^3/\text{sec}, \tag{16}$$

where k_{ox} and k_{red} are characteristic rate factors, which exhibit an Arrhenius type dependence on temperature.

4. CATALYTIC EXHAUST AFTERTREATMENT FOR DIESEL ENGINES

4.1. Oxidation Catalysts for Diesel Engines

Oxidation catalysts in diesel passenger cars were put on the market in 1988. They are presently the preferred emission control system for passenger cars and light duty trucks in Europe as well as for heavy duty diesel engines in the U.S. A diesel oxidation catalyst converts a large part of the hydrocarbon constituents of the SOF, as well as gaseous HC, CO, odor creating compounds and mutagenic emissions. The particulate conversion efficiency is, obviously, much less than the filtration efficiency of a wall-flow filter. However, a particulate control efficiency of even 25–35% is sometimes enough to bring many current development engines within the target range for existing emission standards.[118] The relatively low particulate conversion efficiency is attributed to its limited operating conditions, which are met during engine operation at medium loads. At low loads the exhaust gas temperature is not sufficient to activate the catalyst, whereas at high loads, the SOF part of the particulate, which may be oxidized in the converter, is relatively low.
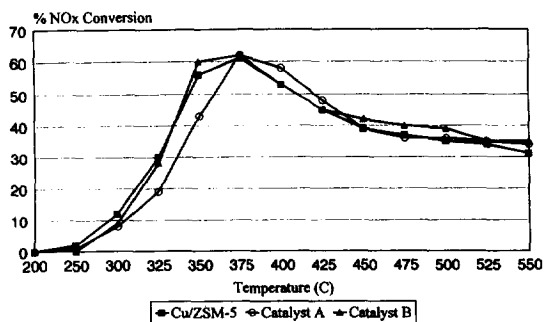
Fig. 18. Activity of zeolite based catalysts as function of temperature. $SV = 50{,}000/hr$, $NO = 1000\,ppm$, $C_3H_6 = 4000\,ppm\,C$, $O_2 = 10\%$, $H_2O = 10\%$, $SO_2 = 50\,ppm$.[127]

The catalyst is also very efficient in reducing emissions of gaseous and particle bound toxic air contaminants, such as aldehydes, PNA and nitro-PNA. While a precious metal catalysed filter would have the same advantages, the catalytic converter has little impact on fuel economy or safety and it will probably not require replacement. Furthermore, in contrast to particulate filters, the catalytic converter is today a relatively mature technology.

A disadvantage of the diesel catalytic converter is potential sulfate emissions. Sulfates can be formed in two ways. For steady-state sulfate formation, the precious metals catalyze the reaction of SO_2 to SO_3, which can further react with water to form sulfates and sulfuric acid.[119] Alternatively, sulfur can be stored as SO_2 or as sulfate on the alumina washcoat.[120] At a certain temperature, the stored sulfur can be released from the washcoat and converted to sulfate (Fig. 17). Efforts have been made to avoid these disadvantages. In order to minimize sulfate production, a silica washcoat is preferred over alumina and Pd is preferred over Pt as the noble metal.[121] On the other hand, as a spinoff from work on selective NO_x reducing zeolite catalysts, some research has been focused on zeolite based diesel catalysts, which decrease the amount of particulate matter by reducing the SOF, and exhibit no significant SO_2 to SO_3 conversion at elevated catalyst temperatures.[122] If the car is driven at elevated exhaust gas temperatures, the catalyst might further oxidize NO to NO_2.[123] Also, at low exhaust gas temperatures, N_2O formation might occur at certain local reducing conditions during engine and catalyst heating.

The tendency of the precious metal catalyst to convert SO_2 to particulate sulfates requires the use of low sulfur fuel: otherwise, the increase in sulfate emissions would more than counterbalance the decrease in SOF. Especially for the application to heavy duty engines, the oxidation catalyst has been formulated to avoid deactivation by poisoning, for example by sulfur oxides in order to match the long service life of these engines. Europe, the U.S. and Japan have already decided to reduce the sulfur content of diesel fuel.

Recent research and development work[124] has led to substantial improvement in the emission performance and durability by use of high precious metal dispersion and narrow particle size distribution on stabilised support systems, which are less prone to thermal sintering and poison uptake. Catalytic activity is further enhanced by use of combined metal oxide promoters, which selectively promote precious metal activity for desired reactions, while still inhibiting SO_2 oxidation and sulfate storage.

4.2. NO_x Reduction Catalysts for Diesel Engines

Much attention has been devoted recently to the reduction of NO_x emissions from diesel engines, that could be made possible by special catalytic exhaust aftertreatment techniques. However, NO_x reduction catalysts and systems suggested for the diesel engines are currently relatively few. The commercial selective catalytic reduction (SCR) catalysts which are currently in use on stationary engines, using reductants such as ammonia or urea, pose great difficulties in their translation to on-road vehicles. The main problems are the additional tank needed for the reductant, its safe transport, its distribution and the potential for the reductant slip, which are not allowed due to safety and health considerations.[125]

A lean NO_x catalyst for diesel engines is required to operate under a wide range of exhaust conditions, depending on the driving mode. The exhaust gas temperatures may vary from $100°C$ for low load cycles to 600–$700°C$ for high load operation. A catalyst, which could be able to promote the NO_x decomposition to nitrogen and oxygen would be ideal, since it would not require any reducing agents. However, even the most promising catalyst reported to date, Cu exchanged ZSM-5[126] is strongly inhibited by O_2 and SO_2 and slightly inhibited by H_2O, all of which are always present in diesel exhaust.

An alternative approach for catalytic conversion of NO_x is the selective reduction using hydrocarbons. The reaction, using propylene as model reactant in this case, is:[127]

$$2NO_x + C_3H_6 + \tfrac{7}{2}O_2 \longrightarrow N_2 + 3CO_2 + 3H_2O. \quad (17)$$
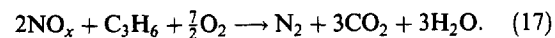
A desired feature of a de-NO_x catalyst is to promote the oxidation of certain hydrocarbons with NO_x instead of oxygen (that is, a high hydrocarbon selectivity).

The current state-of-the-art high temperature catalyst for the selective reduction of NO_x with hydrocarbons in lean environments is Cu/ZSM-5.[128,129] The activity of this catalyst is promoted by the presence of small amounts of O_2, whereas SO_2 and H_2O only slightly inhibit its performance. Unlike precious metals catalysts, which become active at lower temperatures, the zeolite-based Cu/ZSM-5 is active for NO reduction at temperatures above $350°C$ (Fig. 18). A major problem associated with Cu/ZSM-5 is its hydrothermal stability, since it deactivates significantly after steaming for short
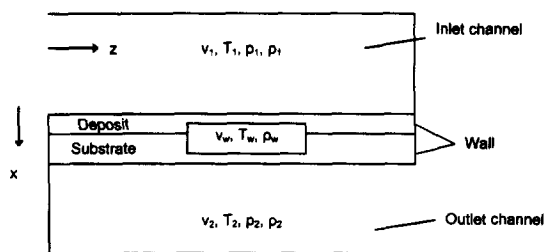
Fig. 19. Schematic diagram of the monolith inlet and outlet channels with the substrate wall and the soot deposit layer.

periods of time at temperatures greater than 700°C. This deactivation is known to be related to zeolite dealumination and subsequent loss in the number of active exchanged Cu cations.[130] The low hydrocarbon selectivity of this catalyst can be compensated by injecting additional hydrocarbon reductants in the exhaust upstream of the catalyst. Due to the very low HC emissions of diesel engines, secondary fuel addition strategy is expected to play a large role in practical application.

Also, it is very important to adapt the catalyst to exhaust gas temperature because whole or only a part of the catalyst contributes to NO_x conversion, depending on the temperature. It has been found that the precious metal catalysts, which have relatively low sulfate suppression ability, can reduce NO_x at low temperatures, but particulate greatly increases by the sulfate formation because of the exhaust gas temperature increase, caused by the addition of secondary fuel. On the other hand, the surplus secondary fuel must be readily oxidized by the catalyst, in order to avoid significant HC and CO emission increases (as is the case with high light-off catalysts). Simultaneous 12% NO_x and 25% particulate reduction have been reported with base metal catalyst by minor optimization of the amount and pattern of secondary fuel addition, with 3% fuel penalty.[129] Higher amounts of secondary fuel are not favorable because they result in an increase of particulate emissions and fuel economy penalty. Furthermore, it is important to note that diesel fuel, which is readily available on diesel powered vehicles, is not the best means of producing the necessary HC for reduction of NO_x. Current research is aimed at the optimization of secondary fuel addition strategies (e.g. by exploitation of the post injection capabilities of modern common rail diesel injection systems), combined with the development of improved catalyst formulations.[131]

5. CATALYSTS FOR DIESEL PARTICULATE FILTERS

5.1. The Particulate Filter

The wall-flow particulate filter (Fig. 19) is today the most efficient device for reducing diesel soot emissions, attaining filtration efficiencies of the order of 90% at nominal operation conditions.[132–135] Soot filtering is especially important in the case of worn-out diesel engines with poorly controlled fuel combustion. Specific application problems, basically related to filter durability, have limited the use of particulate filters, mainly on city buses, some delivery trucks and fork lift trucks. Intensive research is aimed at developing diesel filter systems suitable for a wider application to commercial vehicles or passenger cars.

The particulate filter concept has focused research and development activities around the world, and a variety of systems is offered by various manufacturers.[136,137] A trap oxidizer system is based on a durable temperature resistant filter, which removes particulate matter from the exhaust before it is emitted to the atmosphere. The accumulated particulate raises filter backpressure, i.e. the pressure difference across the filter which is necessary to force the exhaust through it. The typical backpressure level depends on the filter type, and increases as the filter becomes loaded with particulate. High backpressure is undesirable, since it increases fuel consumption and reduces available power. It is necessary to clean the filter periodically by burning off (oxidizing) the collected particulate; this process is known as regeneration.[138]

Under the conditions met in diesel exhaust systems regarding exhaust flow rate and oxygen content, the required reaction rates for complete filter regeneration are attained at temperatures above 550°C. Exhaust temperatures of that order are observed only at high load operation of the diesel engine, which are scarcely attained in the driving cycles of the official tests (e.g. ECE-EUDC, FTP-75 etc.). Thus, special regeneration techniques are employed, that fall into three broad categories:

- thermal regeneration by use of engine measures or by the supply of external energy;
- catalytic regeneration (catalytically coated filter or fuel doping);
- aerodynamic cleaning (using compressed air to remove the soot).

In the first category, a significant fuel consumption penalty must be foreseen to supply the additional energy required for regular thermal regeneration during city driving. Catalytic regeneration, on the other hand, is based on the use of catalysts to achieve the onset of regeneration at significantly lower temperatures. The catalyst may impregnate the porous ceramic wall or be used as a fuel additive, which is emitted and accumulated in the filter together with the particulate. The use of catalysts is critical to the design of a successful diesel filter system, because it overcomes both problems mentioned above: namely that of minimizing backpressure levels and that of sustaining regeneration at low temperatures.[139–145]

The use of some catalytic fuel additives results in regeneration temperatures as low as 350°C, although stochastic regenerations may be observed even down to 200°C for high filter loadings.[143] Figure 20 presents

Fig. 20. Simplified mechanisms of soot and additive deposition and combustion in diesel particulate filters, catalyzed or assisted by the use of additives mixed in the fuel or in the exhaust stream.[146]
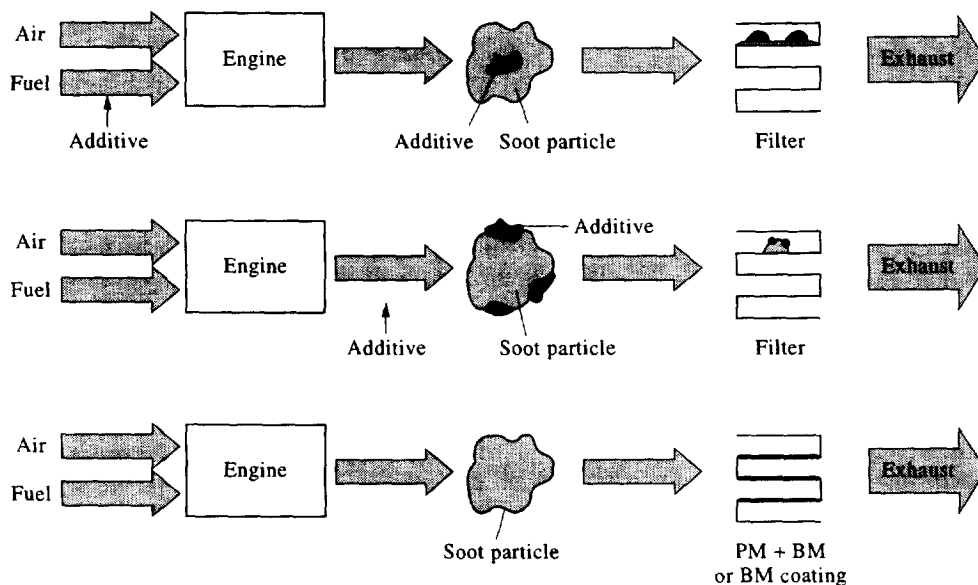
simplified mechanisms of soot and additive deposition and combustion in diesel particulate filters, catalyzed or assisted by the use of additives mixed in the fuel or in the exhaust stream.[146]

5.2. Catalytically Coated Filters

Catalytic coatings on wall-flow filters have not proven very effective in lowering regeneration temperatures. It is well known that even under the most favorable conditions, such as a low exhaust flow rate, high oxygen content and low filter loading, less than 100°C decrease in ignition temperatures is attained.

The experience with catalytically coated filters may be summarized as follows:[147–150]

1. They attain a small reduction in soot ignition temperature (30–100°C). Thus, a thermal regeneration back up device is still needed.
2. The use of precious metal coatings necessitates a very low sulfur content in fuel (ca 0.05% as in the case of catalytic converters).
3. The catalytic coating is more effective with filters with high porosity and mean pore size.
4. Catalytic activity is more pronounced at low filter loadings.
5. Reliability and high life expectancy of the catalytic coating are crucial for the design of a reliable diesel filter system.

In a catalytically coated filter the micro-scale contact, among the carbonaceous particle matrix and the catalyst active sites, is relatively poor. This explains the limited efficiency of these systems in lowering the regeneration temperature as compared to those employing fuel additives.

5.3. Catalytic Fuel Additives

5.3.1. Catalyst types

The most effective application of catalysts in diesel particulate filter systems is based on the mixing of organometallic compounds of various metals in the fuel in very small quantities. The additive is oxidized in the combustion chamber and its oxides form the kernels of particulates, which are collection in the soot layer. A large number of fuel additives have been tested in various applications, based on the following metals: Cu, Mn, Co, Fe, Ni, V, Pb, Ca and Ce.[140–144] In 1986, researchers from General Motors[151] conducted experiments in a laboratory reactor, aiming at calculating reaction kinetic parameters for regeneration by use of Cu, Pb and Mn-based fuel additives. Taking into account the results of TGA analysis, the researchers assumed that the differences in soot reactivity at different temperature levels was due to the different percentage of volatile fraction in the particulate. In 1989, Volkswagen[152] presented experiments based on soot samples collected during a passenger car engine in part and full load conditions, that had been processed with TGA analysis. It was found that the use of fuel additive changes the chemical composition of the soot emitted by the diesel engine.

The use of fuel additives in diesel filter systems may significantly enhance the regeneration frequency, even in city driving. A number of systems have been based exclusively on the use of Mn, Cu or Fe additives.[153,154] Such systems could not attain durability higher than 50,000 km, due to high temperature peaks characterizing the evolution of catalytic regeneration in specific driving modes, known as failure scenarios.[144] In order
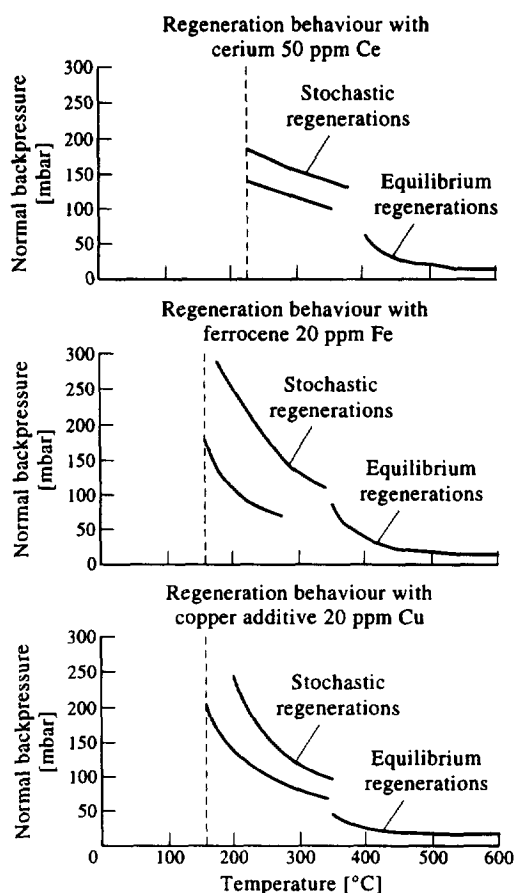
Fig. 21. Regeneration maps for different fuel additives and concentrations: the equilibrium temperature (reaction rate = accumulation rate) is plotted as a function of the normalized backpressure.[143]

to ensure satisfactory durability, the system should be equipped with additional devices to keep filter loading under a specific safety threshold.[145]

5.3.2. Mechanisms of additive action

The process of catalytic regeneration has been extensively studied and a number of models have been developed to understand and predict it. A number of researchers suggested the application of single or multiple stage reaction kinetics for catalytic soot oxidation.[155-158] The results were strongly dependent on the reaction environment.

As mentioned above, in the absence of catalytic assistance, complete filter regeneration occurs at temperatures above 550°C, depending on the exhaust flow rate and prevailing oxygen concentration. Soot ignition at lower temperatures often results in partial combustion of the deposited soot in the filter, leaving behind a less reactive carbonaceous residue. Soot can differ considerably in its reactivity according to the degree of graphitization after partial oxidation and the amount of hydrogen retained. The use of catalytic fuel additives, based on transition metals such as Mn, Cu, Fe, Ce and Pb and finely dispersed[141,159,160]

during the fuel combustion process throughout the soot particles, results in regeneration temperatures as low as 350°C.[132,140,144,161] Although stochastic (erratic) regenerations may be observed even down to 200°C under favorable engine and filter operating conditions (Fig. 21).[143] Minor secondary effects that may arise by the use of catalytic fuel additives include incomplete filter cleaning and filter backpressure increase, due to the retaining of fuel additive ash after regeneration.

Erratic regeneration behavior observed at low temperatures[140,143] has its roots, in part, in the presence of the volatile hydrocarbon. The volatile fraction originates from unburned fuel and lubricating oil and is found adsorbed/condensed on the soot particles at temperatures below 190°C (this part is completely gasified and desorbed at higher temperatures).[132,161] In this case, the regeneration initiates in specific channels of the monolith, where the local soot loading and temperatures are favorable. The associated heat release, apart from the soot, gasifies and ignites the volatile hydrocarbons, thus enhancing the propagation of the reaction. These, unpredictable, low-temperature regenerations may also be 'ignited' by hot particles originating from engine deposits formed by the additive.[143]

Several mechanisms have been suggested to explain the catalytic activity of metal compounds on carbon/soot oxidation/combustion.[162,163] Due to the strong oxygen concentration dependence of the action of transition metal oxides, a redox mechanism[164-168] is usually invoked to explain their catalytic activity: the additive stores and exchanges oxygen atoms with the surrounding carbonaceous matrix and gas. However, additional mechanisms involving catalyzed thermal decomposition of water vapor and soot oxidation by hydroxyl radicals,[164] or electron exchange among additive and carbon atoms resulting in a weakening of the carbon bonds in the boundaries of the carbon matrix facilitating this reaction with oxygen,[162] have also been proposed.

The commonly used transition metal additives for promoting filter regeneration, form more than one type of oxide, corresponding to the possible valence states they can assume. We can, therefore, distinguish between the metal being in 'higher' or 'lower' oxidation state. The approach presented here refers to regeneration catalyzed by transition metal fuel additives, existing as well dispersed oxides with varying valence states inside the porous soot deposit in the filter. Soot oxidation by the catalyst oxides, triggers the ignition of the remaining soot. The fuel additive participates in the combustion process, leaves the combustion chamber and accumulates in the filter together with the emitted soot. Typical filtration efficiencies for additives are usually over 95%.[139,143,161] We can assume that during this process each metal additive molecule is bonded with a number of soot constituents, such as carbon and hydrocarbon molecules. By reaching the filter the metal additive is
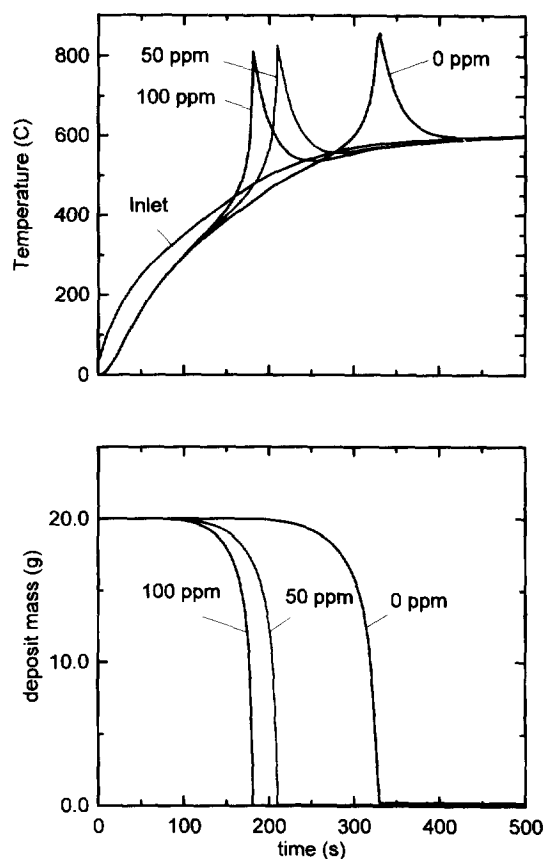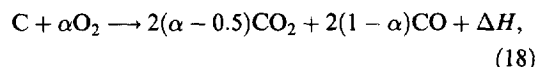
Fig. 22. Comparison of typical filter regenerations with different fuel additive concentrations. Exhaust gas flow rate: 38 g/sec, $[O_2] = 9.3\%$.

dependence of water–CO gas shift reaction. The incomplete carbon oxidation, is assumed to be described by the following reaction:

$$C + \alpha O_2 \longrightarrow 2(\alpha - 0.5)CO_2 + 2(1 - \alpha)CO + \Delta H, \tag{18}$$

α, is an index of the completeness of the reaction taking values from 0.5 to 1. Measured values for soot reported in the literature range between 0.55 and 0.9,[170] while laboratory studies give a value of 0.9 in the absence of water vapor and 0.9–0.975 in the presence of 7% water vapor at 450–300°C, respectively.[169]

Figures 22 and 23 present the computed evolution of filter exit temperature and particulate loading during typical catalytic regenerations with variable catalyst concentrations in the soot layer. The catalytic regenerations are clearly initiated at significantly lower temperatures compared to the thermal (uncatalysed) regeneration. The concentration of additive in the fuel also affects the onset of regeneration. On the other hand, little influence of the catalyst presence in the maximum developed filter temperature is observed. Dimensional analysis of the catalytic regeneration process reveals that the maximum temperature encountered during a catalytic regeneration depends mainly on the soot loading of the filter and to a much lesser extent to other operating parameters.[180]

5.4. Control Issues Related with the Use of Catalysts in Particulate Filters

The durability of regenerable filter systems probably presents the major obstacle in their wider application in vehicle applications. Filter failure may either result from overheating above the melting point or from local high temperature gradients that cause severe thermal and mechanical stresses. This occurs under several failure scenarios, a typical one comprising engine operation at high load and subsequent braking, leading to idle operation with low exhaust flow rates.

Considering the behavior of the regeneration process, we can state four major directions for limiting the undesired high regeneration rates:

1. Maintaining low mean filter loading. According to the results of computation, filter loading substantially affects attainable temperatures during a failure scenario.
2. Cooling of the filter. This would lead to a significant reduction in reaction rates.
3. Reduction of the exhaust gas oxygen content. Again, this would limit reaction rate.
4. Decreasing the exhaust gas residence time in the soot layer.

The above theoretical possibilities could be realized in practice by a number of techniques (limiting filter loading by controlling regeneration frequency, limiting oxygen availability in the

actually in its higher oxidation state. Provided that the filter temperature reaches a sufficiently high value, the metal oxide in the deposit layer releases an oxygen atom to react with soot and assumes its 'lower' oxidation state. The reduced oxides produced in this way may react at the same time with the oxygen contained in the flowing exhaust gas. This continuing oxidation–reduction process, which takes place at significantly lower temperatures than unaided soot oxidation, results in reaction of soot with oxygen from the exhaust gas via the fuel additive, which acts as a catalyst itself.

5.3.3. Soot combustion and CO selectivity

Typical diesel particulate consists mainly of a carbonaceous core (soot formed during combustion), adsorbed components such as unburnt and partially oxygenated hydrocarbons, sulfates (due to the oxidation of the sulphur contained in the fuel) and metal oxides.[132] Laboratory research[169] has shown that CO selectivity of soot oxidation reaction is finite and weakly affected by temperature, to the extent that it can be assumed constant up to 700°C. However, the presence of water vapor introduces a strong dependence on temperature paralleling the temperature
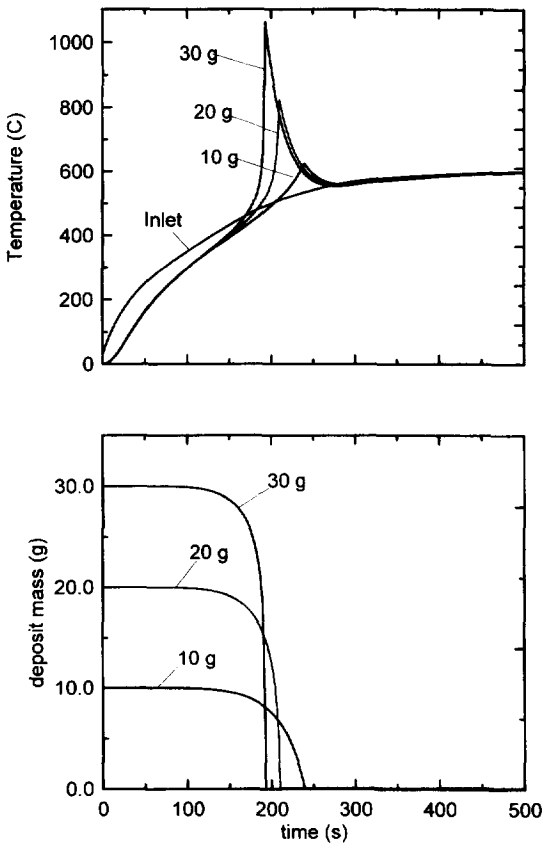
Fig. 23. Effect of initial filter loading on the evolution of filter
temperature during regeneration.

exhaust gas by controlling A/F, filter cooling and
decreased residence time by keeping a high exhaust
flow rate).

As an example, we may consider the principle of
filter protection by limiting the oxygen content of the
feed exhaust gas, which has recently been shown to be
effective in a number of filter failure scenarios.[171]
Figure 24 shows the measured filter inlet and outlet
temperatures developed during a failure scenario
comprising a sudden vehicle braking following
engine operation at high load and speed. This
scenario causes the onset of a very fast regenera-
tion—due to the combination of relatively high
temperatures, low exhaust flow rates and high
oxygen content. In this specific case, exhaust gas
recirculation is activated at $t = 155$ sec in order to
control the regeneration. Lack of regeneration rate
control in this case, would have led to much higher
temperature levels, that could possibly damage the
filter. The experience gained by a significant number
of experiments of this kind, indicates that the design
of a control system for this technique is a complex
task. This is mainly due to the fact that the levels of
exhaust gas recirculation necessary for filter protec-
tion in each specific failure scenario are variable.
Additionally, one must take into account variation in
fuel additive concentration in soot for different filter
loading modes. Control system design in this case is
substantially aided by process modeling.

Filter bypassing by the exhaust gas is an alter-
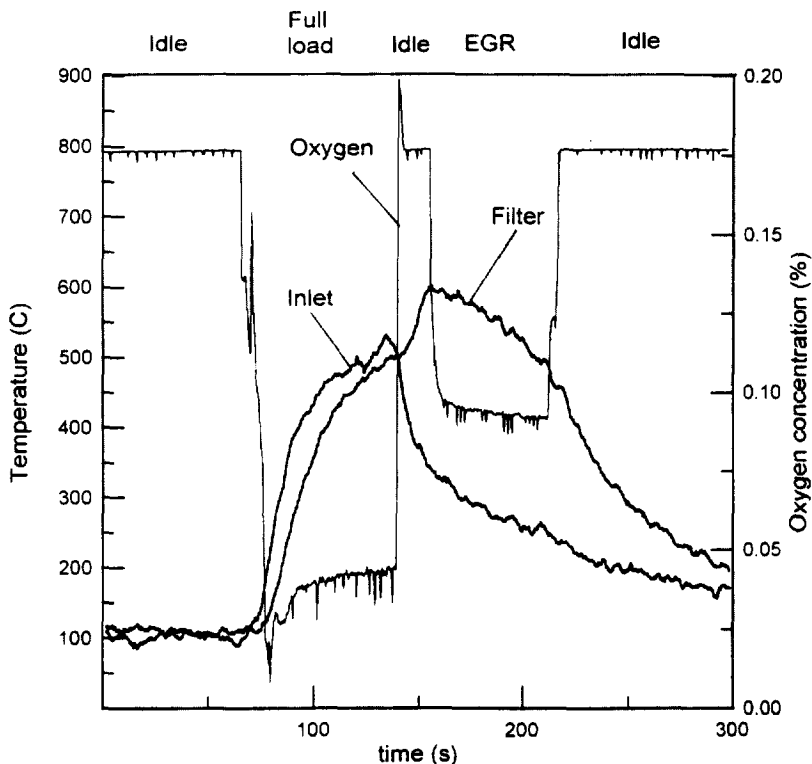native, quite effective protection technique: its

Fig. 24. Filter protection by limiting oxygen content of the exhaust gas during a filter failure scenario.[171]

application has led to high durability of filter systems.[172] Details on different filter protection techniques are given in Stamateios[173] and Pattas et al.[174,175]

5.5. Modeling Catalytic Regeneration

The design of a diesel particulate filter system to fit a specific vehicular application requires significant expenditure, due to the high degree of interaction between the vehicle operation and filter behavior. The assistance of modeling in the design process is already well established.[176]

Zero-dimensional regeneration models for particulate filters assume identical flow conditions of the exhaust gas flowing through the wall along the channel.[177] These models have been quite effective in simulating filter regeneration characteristics under relatively high exhaust flow rates.[178] For operation under low flow rates, variations along the filter channel become significant; so one-dimensional models have been developed for filter thermal (non-catalytic) regeneration.[179]

Existing theories[154,156,158] address catalytic regeneration through phenomenological modifications of the apparent activation energy of soot combustion and frequency factor, employing otherwise unchanged thermal regeneration models. Recently, a zero-dimensional model employing a redox mechanism for fuel additive action in the soot layer has been presented.[180] The model, extended to cover 1-D effects along the filter channel is presented in Koltsakis and Stamatelos.[181] The basic features and balance equations of these types of models are briefly presented below. More details about the model assumptions, the formulation and the solution of the balance equations may be found elsewhere.[179,180]

Figure 19 presents a schematic diagram of the monolith inlet and outlet channels with the substrate wall and the soot deposit layer. The exhaust gas temperatures, densities, velocities and pressures are expressed as radially averaged values. Previous work[177] has shown that conduction in the thin x-direction in the ceramic filter phase is so dominant, that the wall temperature may be taken independent of x, even though the heat from reaction is only produced in the deposit layer. The interphase heat transfer within the wall is so large that the gas and solid temperatures may be taken equal except in a very thin boundary layer at the interface with the inlet channel.

The governing balance equations, along with the correlations used for the pressure drop through the porous monolith wall follow:

conservation of mass of channel gas

$$\frac{\partial}{\partial z}(\rho_i v_i) = (-1)^i (4/D)\rho_w v_w; \qquad (19)$$

conservation of z-component of momentum of channel gas

$$\frac{\partial p_i}{\partial z} + \frac{\partial}{\partial z}(\rho_i v_i^2) = -\alpha_1 \mu v_i / D^2. \qquad (20)$$

The r.h.s. term of Eq. (20) represents the pressure losses in the axial flow direction z, caused by the viscous drag forces. Since the mass flow passing through the wall is only a small fraction of the axial flow, the velocity profile should be close to that observed in flows in closed channels. Thus, the relation used to compute the pressure loss is the one used for laminar flows in square ducts.

Conservation of energy of channel gas:

$$C_{p,g}[D^2\rho_i v_i T_i|_{z+\Delta z} - D^2\rho_i v_i T_i|_z \\ - (-1)^i 4D\Delta z \rho_w v_w T_i|_z] \\ = h_i 4D\Delta z(T_w - T_i). \qquad (21)$$

The overall rate of soot combustion without catalytic aids is assumed to follow a simple Arrhenius type expression:

$$k_1 = kT e^{-E/RT}. \qquad (22)$$

For the apparent activation energy E appearing in Eq. (22) several values have been proposed ranging from 80,000 to 160,000 J/mol.[140,155,156,182,183] Experimental evidence with a Pb additive[184] supports the independence of the apparent activation energy from additive presence, while engine experiments[185] indicate that a value of 150,000 J/mol satisfactory represents regeneration reaction behavior. The concentration of catalyst in the soot layer may be expressed by:[180]

$$\xi = \frac{\text{moles of metal oxides present in soot}}{\text{carbon moles present in soot}}. \qquad (23)$$

The fraction ξ is a function of the metal additive concentration in the fuel as well as the engine soot emissions produced during the filter loading operation. Metal additive oxides can in principle be present in the deposit layer in both the lower and the higher oxidation state. One could define:

$$\psi = \frac{\text{'higher oxidation state' metal oxides present in soot}}{\text{total metal oxides present in soot}}. \qquad (24)$$

During catalytic regeneration the oxidation state of the metal oxides may be changed, by reacting either with oxygen of the exhaust gas or with the carbon atoms of the deposit layer. Thus, if we assume that the metal additive Me forms oxides with say, its 3- and 4-valent states, the following redox reactions take place:

$$2MeO_2 + C \longrightarrow Me_2O_3 + CO \qquad (25)$$

$$Me_2O_3 + \tfrac{1}{2}O_2 \longrightarrow 2MeO_2. \qquad (26)$$
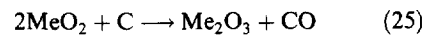
These reactions combine with reaction (18) to complete the reaction scheme for catalytic soot oxidation. They represent a continuous oxidation–reduction process of the metal oxides present in the
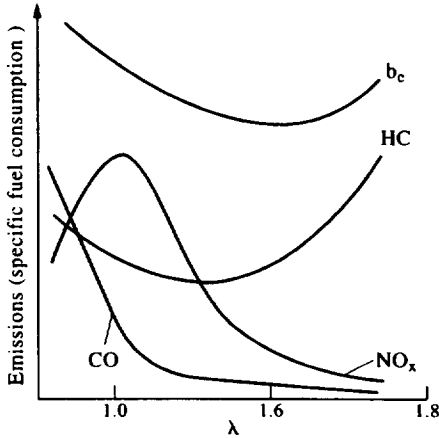
Fig. 25. Lean burn engine raw emissions as a function of lambda [187].

deposit soot layer. The rate of the reduction reaction (25) is assumed to follow an Arrhenius-type temperature dependence according to the following equation:

$$R_{\text{red}} = k_{\text{red}} \cdot \psi \cdot e^{-E_{\text{red}}/RT}. \qquad (27)$$

The rate of the heterogeneous oxidation reaction (26) is expected to be proportional to the oxygen content of the exhaust gas, as well as to the availability of 'lower oxidation state' metal oxides, which is expressed by $1 - \psi$. An Arrhenius-type temperature dependence is also assumed here. The reaction rate for Eq. (27) is then:

$$R_{\text{ox}} = k_{\text{ox}} \cdot [O_2] \cdot (1 - \psi) \cdot e^{-E_{\text{ox}}/RT}. \qquad (28)$$

The total rate of change of ψ may then be written as:

$$\frac{d\psi}{dt} = R_{\text{ox}} - R_{\text{red}}. \qquad (29)$$

Considering the stoichiometry of the reduction reaction the mass balance equation for the deposit layer, assuming that the deposit is consumed in a shrinking mode, gives:

$$\rho_p \frac{dw}{dt} = -\left(\frac{M_c}{M_{O_2}}\right)\rho_w v_w y$$
$$\times \frac{1}{\alpha}\left(1 - \exp\left(-\frac{S_p k_1(T_w)w}{v_w}\alpha\right)\right)$$
$$- \frac{m_b \xi R_{\text{red}}}{2A_f}. \qquad (30)$$

The energy balance equation for the wall should take into account the contributions of convective heat transfer from the channel flow and from the flow through the wall, the heat released by the exothermal soot combustion as well as the conductive heat transfer along the channel wall:

$$\frac{\partial}{\partial t}(\rho_p C_{p,p} T_w + \rho_s C_{p,s} T_w)$$
$$= h_1(T_1 - T_w) + h_2(T_2 - T_w)$$
$$+ \rho_w v_w C_{p,g}(T_1 - T_w) + H_{\text{react}} + H_{\text{cond}}. \qquad (31)$$

From the equation for the consumption rate of the deposit (30), we can compute the heat released by the overall reaction expressed per unit time and area:

$$H_{\text{react}} = \left(-\frac{\Delta H}{M_{O_2}}\right)\rho_w v_w y \frac{1}{\alpha}\left[1 - \exp\left(-\frac{S_p k_1(T_w)w}{v_w}\right)\right]$$
$$- \frac{P_p}{2M_c} W\Delta H\xi R_{\text{red}}. \qquad (32)$$

The contribution of heat conduction is:

$$H_{\text{cond}} = -\lambda_p \frac{\partial}{\partial z}\left(w \frac{\partial T_w}{\partial z}\right) - \lambda_s w_s \frac{\partial^2 T_w}{\partial z^2}. \qquad (33)$$

Darcy's law for the porous ceramic wall as well as for the soot deposit viewed as two porous media in series, is experimentally validated and quantitatively defended for typical filter applications in Sorenson et al.[186] and exploited below to express the pressure 'jump' across the thin cell wall as:

$$p_1 - p_2 = \frac{\mu}{k_p} v_w w + \frac{\mu}{k_s} v_w w_s. \qquad (34)$$

6. CATALYTIC CONVERTERS FOR LEAN BURN SI ENGINES

The lean burn concept has received significant interest by the automobile industry. This is due to the clear advantages concerning brake specific fuel consumption at low engine loads and the relatively lower engine out emissions (Fig. 25).[187] The lean burn engine operates at air-excess conditions at medium loads; when maximum engine torque is desirable, the engine operates at stoichiometric conditions. These engines have intrinsically very low emissions of CO and relatively low HC emissions, that are further reduced by the three way catalyst under oxidizing conditions. In order to meet stringent NO_x emissions standards, in catalyst equipped lean-burn engines, the engine operation is shifted from lean ($\lambda = 1.5$) to stoichiometric ($\lambda = 1$) under high load conditions, e.g. during acceleration and high speed cruising. Thus, although during high load operation, the amount of NO_x is significantly increased, the conventional three way catalysts fed with stoichiometric composition exhaust is capable of keeping low NO_x emissions.

The catalytic reduction of NO in lean exhaust environment presents considerable difficulties, since the reducing CO is present in low concentrations and NO should further compete with oxygen to react with hydrocarbons. Consequently, current lean burn engined vehicles must be run stoichiometrically over a significant part of the legislated driving cycle. New types of catalysts are under development capable of reducing NO_x under lean (oxidizing) conditions. This is achieved by selective reduction of NO_x by HC existing in the exhaust, by use of new
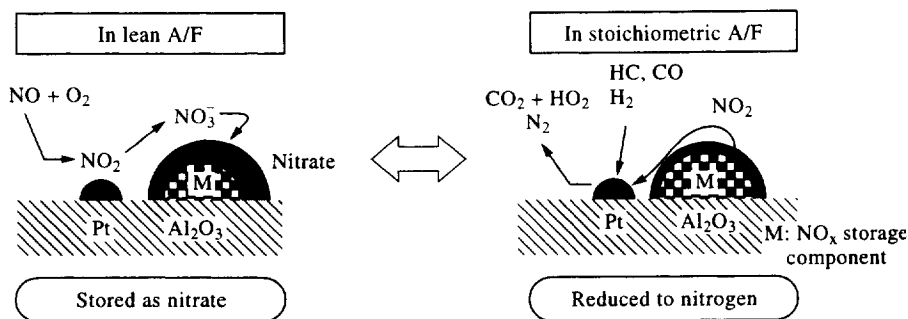
Fig. 26. NO_x storage-reduction mechanism in lean burn NO_x catalysts.[188]

families of catalysts that have been studied recently by a number of researchers,[188-191] with regard to various chemical compound families, including zeolite, alumina and complex oxides. These catalysts, however, posed a number of problems such as low conversion efficiency, narrow temperature window (temperature range where the catalyst has high conversion efficiency) and low heat resistance. In their present status, these types of catalysts are difficult to commercialize and require further development.

The principle of storing NO in the catalyst during lean engine operation and converting it during short duration, carefully controlled, rich excursions was presented and realized in Myoshi *et al.*[188] In a Pt–Ba–Al_2O_3 catalyst, NO was found to be oxidized with oxygen and then react with Ba (storage component) to form a resulting nitrate. The amount of NO storage capacity in such catalysts is strongly affected by the basicity of the elements used as storage components. This is attributed to the fact that the stronger metal basicity results in more stable nitrates. The catalyst was able to reduce NO with CO, H_2 or hydrocarbons, in a similar way as a three-way converter, under stoichiometric or reducing conditions. The NO storage–reduction mechanism is presented schematically in Fig. 26. A lean-burn system with this catalyst and a specially designed fuel control system, that periodically (every 50 sec) caused short (300 msec) enrichments successfully met the Japanese emission standards.

Other researchers used advanced catalysts to expand the lean NO_x reduction capacity of the zeolite catalysts. Takami *et al.*[192] reported a significant increase in NO_x conversion over the legislated U.S. and Japanese driving cycles, by use of Pt–Ir–Rh/MFI zeolite catalysts. These catalysts demonstrated relatively high NO_x reduction performance in a wide operation range from stoichiometric to lean along with a high durability. Their efficiency improved even further by the addition of CeO_2 and Al_2O_3 additives. This catalyst has been mass produced for the Japanese domestic market. However, there is significant work to be done with these catalysts, to increase their efficiency in attaining future, more stringent emissions standards.

7. CONCLUDING REMARKS

This paper reviewed the most common existing catalytic exhaust aftertreatment technologies for gasoline and diesel powered vehicles.

The catalytic technologies were classified according to engine type, which determines the catalyst operating conditions. The stoichiometric Otto engine, which is the most popular today, must be supported by advanced catalyst fast light-off techniques to meet stringent HC emissions standards during cold start. The measures applied to this end should, at the same time, maintain a high durability of the converter.

The diesel engine, which is the second most popular, is under increasing legislative pressure to meet extremely stringent NO_x emissions while keeping very low particulate emissions. A combination of advanced lean NO_x catalysts with diesel particulate filters could be a solution for ultra low emission standards. The well established at present diesel oxidation catalytic converters, although relieved from previous problems with sulfate production, are not capable of sufficiently high particulate emissions reduction.

The lean-burn Otto engine needs further development to meet stringent NO_x emissions levels, without compromising its fuel consumption advantages over the stoichiometric Otto engine.

An outcome of this unified presentation of catalytic exhaust aftertreatment is the fact that the future evolution of vehicle engines is substantially affected by their potential to conform to increasingly stringent pollutant emissions standards. The role of catalyst technologies in this process is essential and causes significant feedback to engine design and control.

Regarding the potential of current catalytic technologies to further improve vehicle tailpipe emissions, it is claimed that substantial gains can be achieved by means of applying system's engineering in the design optimization of exhaust aftertreatment systems. The role of computational models in this field is illustrated by specific application examples and test cases.

It is concluded that the important role of catalyst technologies in meeting the increasingly stringent

vehicle emissions standards will continue for the next decade, strongly affecting the design of engine exhaust aftertreatment systems and the engines themselves.

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