ELSEVIER

Catalysis Today 77 (2003) 419–449

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Automotive catalytic converters: current status and some perspectives

Jan Kašpar*, Paolo Fornasiero, Neal Hickey

Dipartimento di Scienze Chimiche, University of Trieste, via L. Giorgieri 1, I-34127 Trieste, Italy

Abstract

Automotive three-way catalysts (TWCs) have represented over the last 25 years one of the most successful stories in the development of catalysts. The aim of this paper is to illustrate the technology for abatement of exhaust emissions by analysing the current understanding of TWCs, the specific role of the various components, the achievements and the limitations. The challenges in the development of new automotive catalysts, which can meet future highly demanding pollution abatement requirements, are also discussed.

© 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Air pollution generated from mobile sources is a problem of general interest. In the last 60 years the world vehicle fleet has increased from about 40 million vehicles to over 700 million; this figure is projected to increase to 920 million by the year 2010 [1]. The environmental concern originated by mobile sources is due to the fact that the majority of engines employ combustion of fuels derived from crude oil as a source of energy. Burning of hydrocarbon (HC) ideally leads to the formation of water and carbon dioxide, however, due to non-perfect combustion control and the high temperatures reached in the combustion chamber, the exhaust contains significant amounts of pollutants which need to be transformed into harmless compounds. In this paper, the control strategies and achievements in automotive pollution control are discussed. Attention is focussed on recent developments in the field of the three-way type of catalysts, i.e. NM/CeO_2–ZrO_2–Al_2O_3 containing systems; insight on the lean-$DeNO_x$ and diesel type of catalysts is also given. The paper is focussed essentially on the catalytic aspects of pollution abatement, even though the reader should consider that technological solutions such an electrically heated catalysts, etc., may heavily affect the converter performances [2]. A number of review papers have described the traditional CeO_2-based TWC technology, accordingly we refer the reader to these papers [2–13].

2. Emissions characteristics and control strategies

Engine exhausts consist of a complex mixture, the composition depending on a variety of factors such as: type of engine (two- or four-stroke, spark- or compression (diesel)-ignited), driving conditions, e.g. urban or extra-urban, vehicle speed, acceleration/deceleration, etc. Table 1 reports typical compositions of exhaust gases for some common engine types.

---

* Corresponding author. Fax: +39-40-5583903.
E-mail address: kaspar@units.it (J. Kašpar).

0920-5861/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(02)00384-X

Table 1
Example of exhaust conditions for two- and four-stroke, diesel and lean-four-stroke engines [9,155,176,231]

Exhaust components and conditions[a]	Diesel engine	Four-stroke spark ignited-engine	Four-stroke lean-burn spark ignited-engine	Two-stroke spark ignited-engine
NO_x	350–1000 ppm	100–4000 ppm	≈1200 ppm	100–200 ppm
HC	50–330 ppm C	500–5000 ppm C	≈1300 ppm C	20,000–30,000 ppm C
CO	300–1200 ppm	0.1–6%	≈1300 ppm	1–3%
O_2	10–15%	0.2–2%	4–12%	0.2–2%
H_2O	1.4–7%	10–12%	12%	10–12%
CO_2	7%	10–13.5%	11%	10–13%
SO_x	10–100 ppm[b]	15–60 ppm	20 ppm	≈20 ppm
PM	65 mg/m^3			
Temperatures (test cycle)	r.t.–650 °C (r.t.–420 °C)	r.t.–1100 °C[c]	r.t.–850 °C	r.t.–1000 °C
GHSV (h^{-1})	30,000–100,000	30,000–100,000	30,000–100,000	30,000–100,000
λ (A/F)[d]	≈1.8 (26)	≈1 (14.7)	≈1.16 (17)	≈1 (14.7)[e]

[a] N_2 is remainder.
[b] For comparison: diesel fuels with 500 ppm of sulphur produce about 20 ppm of SO_2 [16].
[c] Close-coupled catalyst.
[d] λ defined as ratio of actual A/F to stoichiometric A/F, $\lambda = 1$ at stoichiometry (A/F = 14.7).
[e] Part of the fuel is employed for scavenging of the exhaust, which does not allow to define a precise definition of the A/F.

As shown in Table 1, the exhaust contains principally three primary pollutants,[1] unburned or partially burned hydrocarbons (HCs), carbon monoxide (CO) and nitrogen oxides (NO_x), mostly NO, in addition to other compounds such as water, hydrogen, nitrogen, oxygen, etc. Sulphur oxides, though polluting, are normally not removed by the post-combustion treatments, since the only effective way is to reduce them to elemental sulphur, which would accumulate in the system. Accordingly, it is preferred to minimise sulphur emissions by diminishing the sulphur content in the fuel. Given the different nature of the three classes of pollutants, i.e. reducing or oxidising agents, it is necessary to simultaneously carry out both reduction and oxidation reactions over the exhaust catalyst, which can occur by a variety of reactions. Some of these are summarised in Table 2. Importantly, this table reports only the desirable reactions, in that many other reactions could occur in the complex mixtures described in Table 1, such as, for example, reduction of NO_x to ammonia, partial oxidation of HC to give aldehydes and other toxic compounds, etc. Given the complexity of the exhaust media, a high selectivity is required in order to promote only the reactions reported in Table 2.

A perusal of the exhaust compositions reported in Table 1 for the different type of engines reveals some significant differences: (i) even if relatively diluted, the concentration of the various pollutants can change even by an order of magnitude, according to the type of engine; (ii) with the exception of the four-stroke spark ignited-engine, which, being equipped with a TWC, is run at stoichiometry, the other type of engines can be run under lean conditions, i.e. in excess of O_2; (iii) extremely high temperatures are reached in the four-stroke spark ignited-engine, particularly in the close-coupled catalyst (CCC).

In general, the emissions depend on air-to-fuel (A/F) ratio, as exemplified in Fig. 1. Tuning of the engine to rich feed gives the highest power output, which, however, occurs at expenses of high fuel consumption. Under lean conditions lower combustion

Table 2
Reactions occurring on the automotive exhaust catalysts, which may contribute to the abatement of exhaust contained pollutants [4]

Oxidation	$2CO + O_2 \rightarrow 2CO_2$ $HC + O_2 \rightarrow CO_2 + H_2O$[a]
Reduction/three-way	$2CO + 2NO \rightarrow 2CO_2 + N_2$ $HC + NO \rightarrow CO_2 + H_2O + N_2$[a] $2H_2 + 2NO \rightarrow 2H_2O + N_2$
WGS	$CO + H_2O \rightarrow CO_2 + H_2$
Steam reforming	$HC + H_2O \rightarrow CO_2 + H_2$[a]

[a] Unbalanced reaction.

---

[1] The ability of the TWCs to simultaneously eliminate three classes of pollutants is at the origin of their name.

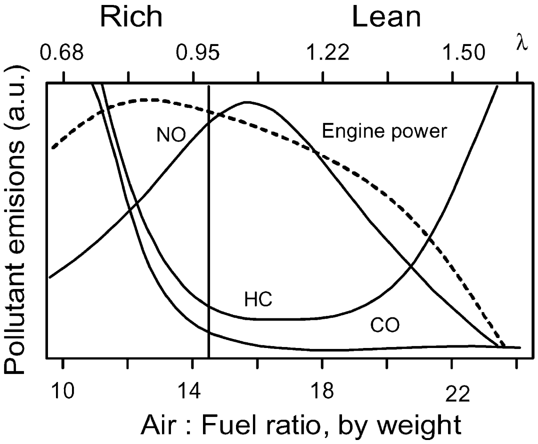

Fig. 1. Effect of A/F ratio (w/w) on engine emissions and engine power (after Ref. [3]).

temperatures lead to lower NO_x emissions, however, at very high A/F engine misfire occurs, leading again to high HC emissions. Under any A/F conditions catalytic abatement of pollutants is needed to comply with the legislation limits. Only at stoichiometric conditions are appropriate amounts of reducing and oxidising agents present in the exhaust to carry out the catalytic reactions as outlined in Table 2. Under such conditions TWCs effectively remove the pollutants.

In principle, there are several advantages in removing NO_x from the automotive exhaust under lean conditions, i.e. A/F $>$ 14.7, compared to the stoichiometric feed (A/F $=$ 14.7) of a traditional gasoline-fuelled engine, where the polluting components are abated using a TWC. The most important advantage of lean-burn engines is the significant fuel economy. In fact, an increase of fuel consumption of vehicles occurred in the 1990s, which was generally attributed to the introduction of TWCs and their requirement for a stoichiometric A/F ratio to achieve best performances. However, it should be noted that there are other factors that substantially contributed as well, such as the increase of vehicle weight due to implementation of security systems, the generalised use of vehicle air conditioning, etc. There is another advantage of lean NO_x engine, which is the fact that the highest exhaust temperatures are typically lower ($\leq$800–850 °C) compared to the stoichiometric engines. In the latter engine, temperatures up to 1100 °C are met by the CCC, which may result in a disadvantage in terms of the catalyst durability.

Three types on engines can effectively run under lean-burn, i.e. diesel, four-stroke/lean-burn and two-stroke engine. The two-stroke engine is typically employed in small motorcycles, mopeds, chain saws and most recreational vehicles. This engine is characterised by high engine power output, compact design, and low construction costs, which makes it ideal for the above listed applications. However, it is noisy, it presents high fuel consumption and high levels of emitted HCs due to partial mixing of the combustion mixture with the exiting exhaust. It is estimated that up to 25–30% of fuel in the feed is emitted during the scavenging process of the exhaust mixture from the cylinder [14]. Accordingly, the HC emitted from this engine are predominantly C5–C6, in contrast to all other engines where C1–C3 constitute the majority of HC emitted. Even though various strategies of engine management were developed for limiting such high HC emissions, pollution control by catalytic methods is nowadays mandatory even for these engines, which may be achieved by introducing an oxidation catalyst for CO and HC removal, as the legislation is generally less demanding compared to four-wheel vehicles. Due to the intrinsically low NO_x emission levels (Table 1), EGR (exhaust gas re-circulation) technology can be employed for the reduction of emitted NO_x. Should legislation significantly increase the tightness of the present and forecasted limits, it may be expected that four-stroke engines, equipped with conventional TWCs could gradually replace two-stroke engines, as happened for four-wheel vehicles.

As for the exhausts originated by diesel and lean-burn engines, let us observe that even though both types of engines run in an excess of oxygen, typically 5–15% of O_2 is present in the exhausts compared to approximately 1% found in the engine fed at stoichiometry; the precise nature of the exhaust gases significantly differs between the two systems. In fact, both types of engine emit HC and NO_x at ppm levels (300–800 ppm) and large amounts of O_2 (5–15%), water and CO_2 (each 10–12%). However, as far as the HCs are concerned, there is an important difference in that very low levels are emitted from the diesel engine ($\leq NO_x$), which makes necessary addition of a reducing agent to the exhaust in order to achieve appreciable reduction of the emitted NO_x. On the other hand, diesel emissions are characterised by a significant level of particulate matter, which itself can be employed as a reducing agent for NO_x, or, vice versa, particulate can be abated by using NO_x as oxidant as in Johnson Matthey's continuously regenerating trap (CRT) [15]. In contrast, the issue of particulate matter is absent in the case of lean-burn engine powered by gasoline; moreover, higher contents of HC are emitted, which, in principle, allows direct selective catalytic NO_x removal to occur. In addition to these differences in the nature of the exhaust gases, the range of exhaust temperatures strongly differ between the two types of engine. For diesel exhaust, temperatures are on average in the range of 80–180 °C under the European urban driving cycle with some maxima up to 230 °C, while in the extra-urban part of the testing cycle a maximum temperature of 440 °C was observed, typical temperatures being in the range 180–280 °C [16]. This represents a serious problem, both in terms of need of activity at low temperatures and the difficulty in de-sulphurisation of the catalysts, which generally requires temperatures above 650 °C.

Let us now focus on the four-stroke spark ignition engines equipped with TWCs. As above reported, the required amounts of reducing and oxidising agents are present in the exhaust only under stoichiometric conditions. This leads to the typical dependency of the conversion patterns of the TWCs upon the A/F ratio (Fig. 2). Today the required conversion of pollutants is greater than 95%, which is attained only when a precise control of the A/F is maintained, i.e. within a narrow operating window. Accordingly, a complex integrated system is employed for the control of the exhaust emissions, which is aimed at maintaining the A/F ratio as close as possible to stoichiometry (Fig. 3). To obtain an efficient control of the A/F ratio the amount of air is measured and the fuel injection is controlled by a computerised system which uses an oxygen (λ) sensor located at the inlet of the catalytic converter. The signal from this λ sensor is used as a feedback for the fuel and air injection control loop. A second λ sensor is mounted at the outlet of the catalytic converter (Fig. 3). This configuration constitutes the basis of the so-called engine on-board diagnostics (OBD). By comparing the oxygen concentration before and after the catalyst, A/F fluctuations are detected. Extensive fluctuations of A/F at the outlet signal system failure. This OBD arrangement implicitly assumes that a narrow A/F window at the stoichiometric point is the fingerprint of an effective TWC system.

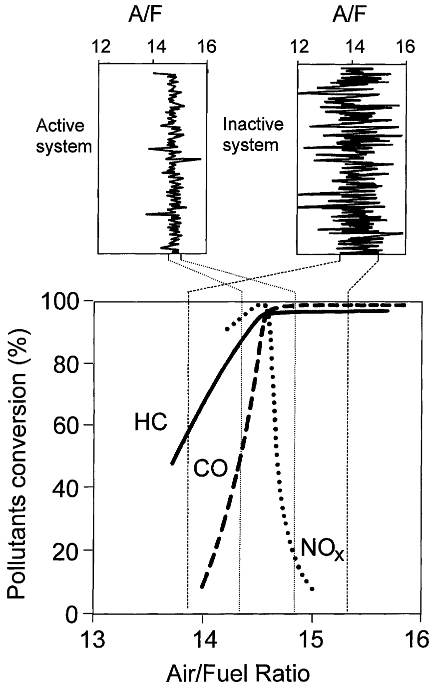

Fig. 2. Effect of A/F ratio on the conversion efficiency of three-way catalysts.

The location of the catalytic converter is another critical point which determines the conversion efficiency. TWCs typically feature the so-called light-off type conversion vs. temperature behaviour. This curves is characterised by conversion which steadily increases from 0 to 100% conversion, the temperature

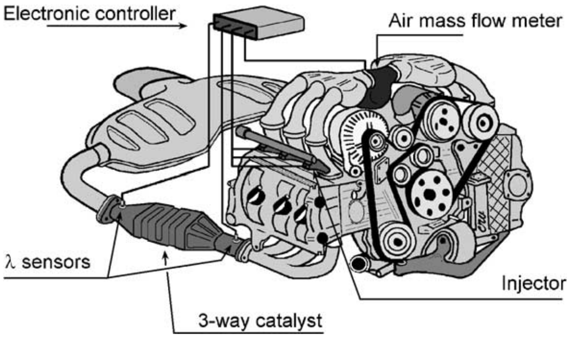

Fig. 3. Diagram of a modern TWC/engine/oxygen sensor (λ) control loop for engine exhaust control.

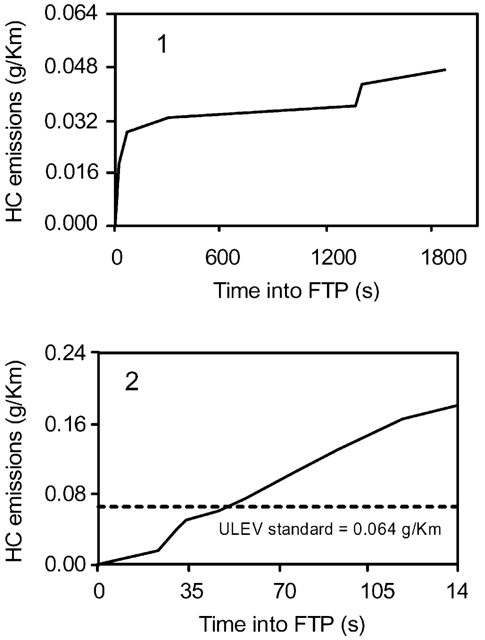

Fig. 4. Cumulative HC emissions measured during the federal test procedure (FTP cycle) on an US 1995 car: (1) tailpipe emissions with CCC; (2) engine-out emissions (after Ref. [11]).

of 50% of conversion being indicated as the light-off temperature. TWCs are characterised by a light-off temperature around 250–350 °C. This means that an under-floor catalyst is heated above the light-off temperature within 90–120 s. In contrast, when the catalyst is closely coupled to the engine (CCC) the heating time typically drops down to 10–20 s. This dramatically affects vehicle emissions immediately after the start-up of the engine (Fig. 4). As shown in this figure, the ULEV (Californian ultra-low emissions vehicle) limit (0.064 g HC emitted/km) is typically surpassed within 40 s after the engine start-up (Fig. 4(2)) [11]. To avoid this situation an almost instantaneous heating of the converter is required to achieve the required >95–98% conversion. CCCs minimise the heating time, however, temperatures up to 1100 °C are routinely met as a consequence of this location of the catalyst.

It must be realised that the latest US and European legislation (EURO phase V and US TIER II) limits for automotive emissions require application of the CCCs and OBD technologies in order to meet the emission standards. A high durability is also an important requirement for present and future TWCs, for example a durability up to 120,000 miles of the converter will be demanded by US tier II regulations in 2004. It should be considered that if a significant part of the vehicle fleet fails the periodical exhaust emission control test, converter replacement becomes mandatory for a vehicle manufacturer. Accordingly, an extremely efficient and robust catalyst is required for future vehicle application. In summary, catalytic converters suitable for 2005 and beyond must present the following characteristics:

- High activity and selectivity (conversions >98%) which increases up to 99% for Californian SULEV (super ultra-low emission vehicle).
- Very fast light-off (<10–20 s), i.e. high activity at low temperatures.

In the case of vehicles equipped with TWCs, two additional requirements should be considered:

- high thermal stability;
- high oxygen storage capacity.

Amazingly, problems and needs for improvements such as those above listed have been quoted for many years when discussing TWCs. A question arises: Why have they not been solved as yet? The reason is that as the performances of the TWCs improve, higher and higher targets, e.g. decrease of emissions and increase of durability, are pushed forward by the legislators, asking for further improvement of the de-pollution technology. For example, starting from 2003 the California SULEV legislation will require a 10-fold decrease in NO_x emissions compared to the already tight value of ULEV legislation (0.2 g/km), whereas HC emissions should drop by a factor of four, down to 0.01 g/km, with converter durability as high as 120,000 miles. Typically, cumulative tailpipe emissions exceed such stringent values within 3–15 s from the start of the engine! This means that catalyst must be effective a few seconds before this limit is reached and convert nearly 100% during the remaining period of the test procedure.

3. TWCS: principles and operation

A typical design of a modern three-way catalytic converter is reported in Fig. 5. Basically, it is a stainless

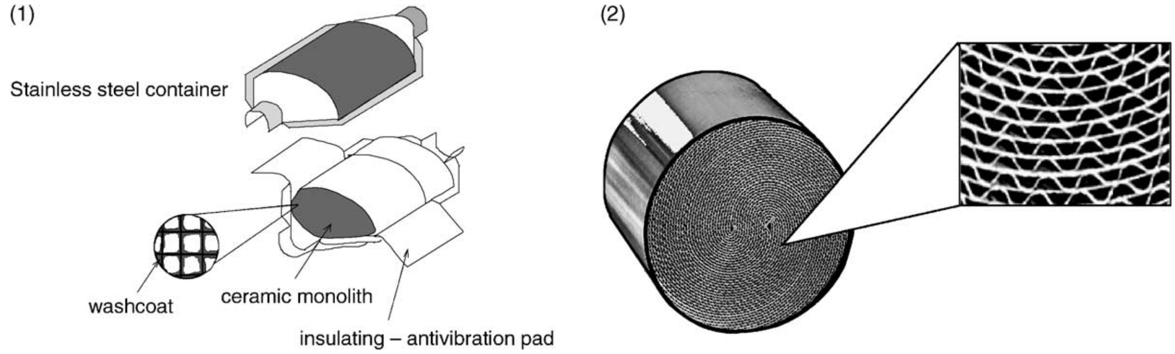

Fig. 5. Diagram of a typical catalytic converter (1) and a metallic honeycomb (a monolith from Emitec GmbH; adapted with permission) (2).

steel container which incorporates a honeycomb monolith made of cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) or metal [9]. Although this aspect is sometimes neglected in the scientific literature, in must be underlined that the choice and geometrical characteristics of the honeycomb monolith play a key role in determining the efficiency of the converter. In fact, high conversion must be achieved in the converter and therefore the catalyst works under conditions where severe mass and heat transfer limitations apply. Typically, both metal and ceramic monoliths are employed nowadays. The major advantage of the metallic substrate is that the wall thickness is limited by the steel rolling mill's capabilities, not strength. In a typical automotive 400 cell/in.^{2} application, the frontal flow area in a ceramic monolith is 69% open (31% closed), while the metallic version has 91% open area. This is due to the higher wall thickness of ceramic monoliths (0.007 in. (0.178 mm)) compared to metallic ones (0.002 in. (0.050 mm)) [17,18]. However, even in this field there has been a strong improvement of the technology, cell densities as high as 900 cell/in.^{2} or even higher are now commonly available on the market for both types of monoliths [19]. Traditionally, cordierite monoliths have been employed quite extensively, primarily due to their lower production cost. However, a major advantage of the metal monoliths resides in their high thermal conductivity and low heat capacity, which allow very fast heating of the CCCs during the phase-in of the engine, minimising the light-off time.

The monolith is mounted in the container with a resilient matting material to ensure vibration resistance [10,20]. The active catalysts is supported (washcoated) onto the monolith by dipping it into a slurry containing the catalyst precursors. The excess of the deposited material (washcoat) is then blown out with hot air and the honeycomb is calcined to obtained the finished catalyst. This is clearly a very simplified and schematic description of the washcoating process as multiple layer technology, or multiple catalyst-bed converters are also employed [10,21]. The exact method of deposition and catalyst composition is therefore highly proprietary and specific for every washcoating company. For example, the metallic honeycombs are non-porous, which makes adhesion of the washcoat difficult. Accordingly a FeCrAl based alloy is employed, which contains up to 5 wt.% of aluminium; after an appropriate pre-treatment this element then acts as an anchoring centre for adhesion of the washcoat [19].

However, there are some common components, which represent the state-of-art of the washcoating composition:

- Alumina, which is employed as a high surface area support.
- CeO_2–ZrO_2 mixed oxides, principally added as oxygen storage promoters.
- Noble metals (NM = Rh, Pt and Pd) as active phases.
- Barium and/or lanthana oxides as stabilisers of the alumina surface area.

3.1. Al_2O_3

The choice of Al_2O_3 as carrier is dictated by the necessity of increasing the surface area of the honeycomb monolith which is typically below 2–4 m^2 l^{-1}, where the volume is that of the honeycomb [22]. This does not allow achievement of high NM dispersion. Alumina is chosen due to its high surface area and relatively good thermal stability under the hydrothermal conditions of the exhausts. In most of the studies γ-Al_2O_3 is employed due to its high surface area with respect to other transitional aluminas [23], however, also other high temperature aluminas such as δ- and θ-Al_2O_3 can be employed for high temperature applications such as in the CCCs because of their high thermal stability compared to γ-Al_2O_3. Since temperatures above 1000 °C can be met in the TWCs, stabilisation of transition aluminas is necessary to prevent their transformation to α-Al_2O_3, which typically features surface areas below $10\,m^2\,g^{-1}$. A number of stabilising agents have been reported in the literature, lanthanum, barium, strontium, cerium, and more recently, zirconium oxides or salts being the most investigated [24–31]. These additives are impregnated onto γ-Al_2O_3 or, sometimes, sol–gel techniques are employed to improve the stability of the surface area. The exact mechanism by which these additives stabilises transitional aluminas strongly depends on the amount of the stabilising agent and the synthesis conditions. This is exemplified in Fig. 6 for BaO doped aluminas; BaO and lanthana are the most used and effective stabilisers.

The effectiveness of each dopant on the stabilisation of alumina is difficult to predict, due to the variability of the factors involved in the synthesis. For example, CeO_2 was shown to thermally stabilise Al_2O_3, the maximum stabilisation effect being attained at a CeO_2 level of 5% [32]. However, Morterra et al. [33,34] found that little stabilisation of BET areas is attained by adding CeO_2 to γ-Al_2O_3, even though significant modification of surface properties were detected. In fact, using CO as a surface probe molecule of the surface Lewis acidity of the CeO_2–Al_2O_3 mixed systems, it was revealed that CeO_2 accumulates preferably on the flat patches of low-index crystal planes of the spinel structure, and that the presence of Ce cations stabilises, also at high temperatures, the most acidic Lewis centres. A possible rationale may be given by the recent observation that very efficient stabilisation of Al_2O_3 by addition of CeO_2 is achieved under reducing conditions compared to the oxidising ones, due to formation of $CeAlO_3$ [31]. Apparently, the stabilisation effect is more pronounced as long as dispersed Ce^{3+} species are present at the Al_2O_3 surface. The presence of such species has long been detected in CeO_2–Al_2O_3 provided that low CeO_2 loading is employed [35,36]. It is conceivable that CeO_2 stabilises γ-Al_2O_3 in a similar fashion to La^{3+}, i.e. formation of a surface perovskite-type of oxide $LaAlO_3$ [24], which may account for the conflicting observations reported in the literature. Under high temperature oxidising conditions, partial re-oxidation of Ce^{3+} sites may occur, with formation of CeO_2 particles which tends to agglomerate and grow over the Al_2O_3 surface, making stabilisation ineffective.

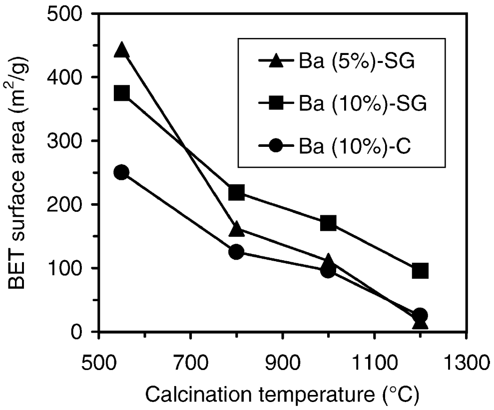

Fig. 6. Effect of synthesis method and BaO content of the stability of BET areas of Al_2O_3 after calcination at the indicated temperatures for 3 h. SG: sol–gel synthesis method; C: co-precipitated sample (after Ref. [29]).

Use of ZrO_2 has also been reported to effectively stabilise γ-Al_2O_3 at high temperatures [25]. In this case, however, the stabilisation of Al_2O_3 seems to be related to the ability of ZrO_2 to spread over the Al_2O_3 rather than formation of mixed oxides. Even though formation of ZrO_2–Al_2O_3 solid solution has been sometimes claimed, separation into ZrO_2 and Al_2O_3 occurs upon high temperature calcination, as dictated by the phase diagram [37]. The effectiveness of ZrO_2 in improving the thermal stability of Al_2O_3 surface area seems remarkable as surface areas as high as $50\,m^2\,g^{-1}$ were observed after calcination at 1200 °C [25]. Interestingly, ZrO_2 appears to be more effective than CeO_2 in stabilising Al_2O_3; consistently, ZrO_2-rich CeO_2–ZrO_2 mixed oxides more effectively stabilised Al_2O_3 compared to CeO_2-rich systems [30].

The overall picture concerning the development of Al_2O_3-based supports is that, at present, thermal stability of the Al_2O_3 support is not an important issue for the next generation of TWCs in that the progress obtained so far makes these stabilised supports suitable even for high temperature applications such as in CCCs.

3.2. CeO_2–ZrO_2 mixed oxides

The beneficial effects of CeO_2-containing formulations of the TWC performances has long been recognised [38]. Many different promotional effects have been attributed to this component, such as the ability to:

- promote the noble metal dispersion;
- increase the thermal stability of the Al_2O_3 support;
- promote the water gas shift (WGS) and steam reforming reactions;
- favour catalytic activity at the interfacial metal-support sites;
- promote CO removal trough oxidation employing a lattice oxygen;
- store and release oxygen under, respectively, lean and rich conditions.

A detailed discussion of these roles and their relative importance is beyond the scope of this work and for this we refer the reader to earlier literature [4,12,13].

Among the different roles of CeO_2 in TWCs, the OSC is certainly the most important one, at least from the technological point of view. In fact, as above discussed, the OBD technology is based on monitoring of the efficiency of the OSC. This is due to the fact that unambiguous relationships between the TWC activity and OSC performances have been established [39]. For this reason, we will principally discuss thermal stability and the OSC property of the CeO_2–ZrO_2 mixed oxides, even though the reader should be aware that a variety of complex phenomena occur under the real exhaust conditions, originated mainly by the interaction of the NM- and CeO_2-based materials.

Starting from 1995, CeO_2–ZrO_2 mixed oxides have gradually replaced pure CeO_2 as OSC materials in the TWCs [40], even though some low purity CeO_2 materials may be employed for less demanding TWC technologies [41]. The principal reason for the introduction of CeO_2–ZrO_2 mixed oxides in place of CeO_2 is due to their higher thermal stability, as exemplified in Fig. 7, which reports the OSC and BET area of CeO_2–ZrO_2 mixed oxides as a function of CeO_2 content [42]. Clearly, there is an important improvement of both OSC and BET area as soon as ZrO_2 is inserted into the CeO_2 lattice. At first glance, there appears to be a straightforward indication in Fig. 7, that is, CeO_2-rich compositions (around 60–70 mol%) are the most effective OSC promoters for TWC application. Unfortunately, this is a very simplified view of the problems related to the use of CeO_2–ZrO_2 mixed oxides in the TWCs, the real situation being much more complex, as described below.

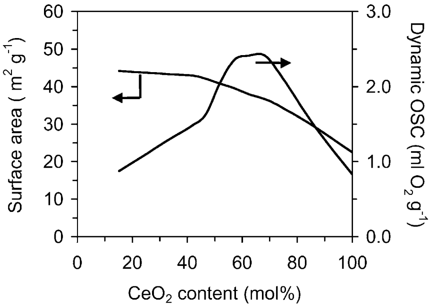

Fig. 7. Effect of CeO_2 content on the surface area stability and dynamic-OSC of CeO_2–ZrO_2 after calcination at 900 °C. OSC measured at 400 °C by alternatively pulsing 2.5% O_2 in He and 5% CO in He over the catalyst (after Ref. [42]).

3.2.1. Thermal stability of CeO_2–ZrO_2 mixed oxides

Thermal stability of the TWCs has always been a major issue in the development of the TWCs. The increase of the cruised mileage of passenger cars and higher exhaust temperatures observed nowadays compared to past [1], demanded for higher and higher thermal stability of the washcoat and particularly of the CeO_2 component. The relationship between the extent of surface area of CeO_2 and the OSC property, as detected by temperature programmed reduction (TPR), is well established (see Fig. 8 as an example). As below discussed, the ability of CeO_2 to undergo reduction, i.e. release of oxygen, at low temperatures (<500 °C) is well recognised as an immediate and useful tool to detect deactivation of the OSC and hence of TWC activity. Accordingly, the primary target in the development of high temperature OSC materials was always considered the resistance of CeO_2 towards sintering.

In principle, there are a number of different routes which may lead to enhanced thermal stability of the

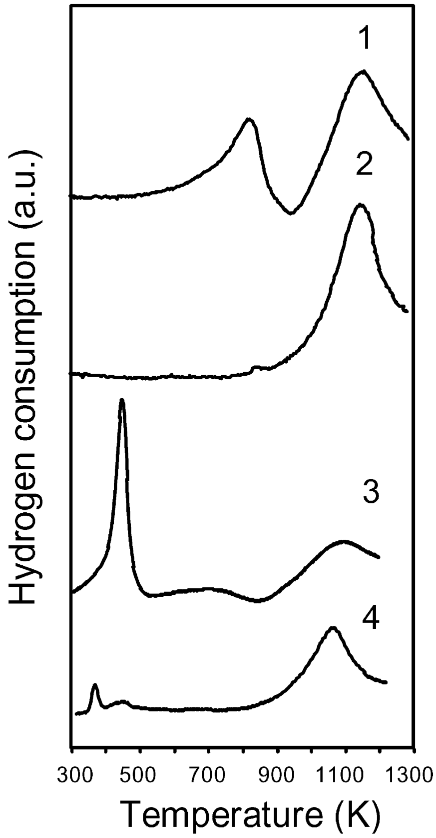

Fig. 8. TPR profiles of CeO_2 ((1) and (2)) and Rh/CeO_2 ((3) and (4)) with surface areas of, respectively, $190\,m^2\,g^{-1}$ ((1) and (3)) and $<10\,m^2\,g^{-1}$ ((2) and (4)).

CeO_2-based materials, which may be summarised as follows: (i) design of microstructure/textural properties by adopting an appropriate synthesis methodology, (ii) appropriate doping of CeO_2, (iii) dispersing of CeO_2 on a carrier. This last aspect has already been partially addressed since it is particularly related to the thermal stabilisation of Al_2O_3 (see above), as synergic stabilisation effects have been found for the CeO_2–ZrO_2–Al_2O_3 system [30]. Of course, any combination of these strategies can also be adopted, however, for sake of simplicity we prefer to discuss these aspects ((i) and (ii)) separately.

3.2.1.1. Design of microstructure/textural properties. The sinterability of any material is clearly related to its textural properties and in particular to its pore structure [43]. The pore structure, in turn, strongly depends on the synthesis conditions. For example, co-precipitation is typically employed to prepare mixed oxide catalysts. It has been shown that when the precipitated cake is treated at 80 °C in the presence of surfactants, extensive mesoporous texture develops in the CeO_2–ZrO_2 mixed oxides, leading to remarkably high surface areas compared to the traditional co-precipitation route [44]. On the other hand, the sintering mechanism at high temperature was apparently little affected, as comparable loss of surface area, in terms of relative loss of BET area, was observed in both samples, independently of the synthesis method [40]. Generally speaking, as the sintering at high temperatures proceeds, annihilation of small pores occurs first leading to decreases of the cumulative pore volume and BET area. On the other hand, large pores sinter with more difficulty as longer migration distances are needed for the matter to fill the pores and sinter the material. This concept is clearly illustrated by results of calcination of two $Ce_{0.2}Zr_{0.8}O_2$ samples where appropriate modifications of the conditions of sample processing were applied in a controlled way to obtain the initial pore distribution shown in Fig. 9. As a result of this pore distribution, sample A features a surface area of $27\,m^2\,g^{-1}$ after calcination at 700 °C, which decreases by 85% after calcination at 1000 °C for 5 h, giving a BET area of $4\,m^2\,g^{-1}$. This is not a surprising result since BET area of few square meters per gram are typically found after such a harsh calcination [45,46]. Sample B features much larger pores compared to sample A, leading to a BET surface area of $35\,m^2\,g^{-1}$ after calcination at 700 °C. However, when the calcination temperature is increased to 1000 °C, a relatively small decrease of the BET area (37%) is observed, as the obtained product features a BET area of $22\,m^2\,g^{-1}$. This is perfectly in line with the above reported comments on the sintering behaviour and indicates that extreme care should be taken before the effects of variation of CeO_2–ZrO_2 composition on textural stability can be assessed. Clearly, *meaningful comparison of properties of* CeO_2–ZrO_2 *mixed oxides can be obtained only when samples of comparable textural properties are compared.*

3.2.1.2. Doping of CeO_2–ZrO_2 *mixed oxides with other elements.* Even though the introduction of CeO_2–ZrO_2 mixed oxides into the TWCs represented a significant breakthrough point compared to the

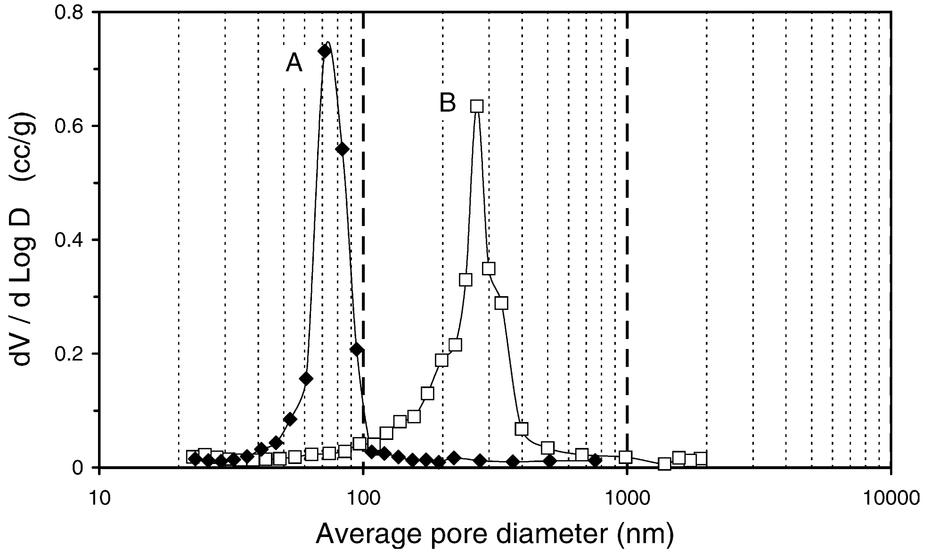

Fig. 9. Pore distribution in two samples of $Ce_{0.2}Zr_{0.8}O_2$ as detected from N_2 desorption isotherm using the BJH method: (A) surface area $= 27\,m^2\,g^{-1}$; (B) surface area $= 35\,m^2\,g^{-1}$.

CeO_2-based technology, it is now recognised that undoped CeO_2–ZrO_2 do not present sufficient thermal stability for application on the 2005 type of TWC converters. In fact, thermal stability in excess of 1000 °C cannot be achieved by simple CeO_2–ZrO_2 due to their metastable nature. As shown in the phase diagram reported in Fig. 10 [47–50], there are metastable (t' and t'') phases at intermediate CeO_2 compositions, which upon heating under oxidising conditions, lead to phase separation, CeO_2-rich (cubic: c-$Ce_{0.8}Zr_{0.2}O_2$) and ZrO_2-rich (tetragonal: t-$Ce_{0.2}Zr_{0.8}O_2$) phases being typically obtained [51,52]. In principle, TWCs must show high durability; accordingly phase separation is considered an undesirable feature of the CeO_2–ZrO_2 component since it may lead to unpredictable variations in the properties of the catalyst. By analogy with ZrO_2, trivalent dopants, such as yttria and lanthana, have been employed for the CeO_2–ZrO_2 mixed oxides [53–58]. However, to our knowledge no systematic study satisfying the above reported criterion of comparable textural properties for comparison of effects of composition has been reported so far. This makes difficult a rationalisation of the data reported in the literature on the effects of the doping agents.

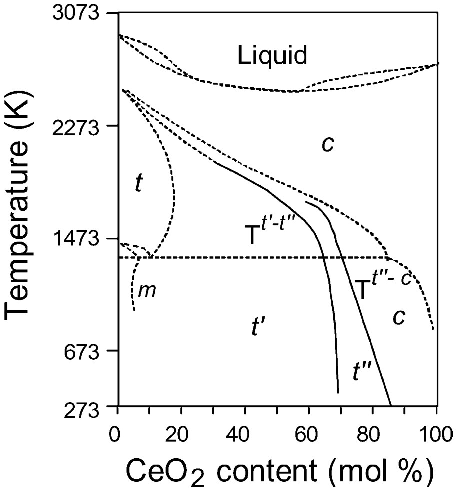

Fig. 10. Experimental phase diagram of the CeO_2–ZrO_2 system (after Ref. [70]).

Some qualitative and general comments can, however, be made for CeO_2–ZrO_2 systems: (i) CeO_2–ZrO_2 phase separation is favoured at the intermediate compositions and it is retarded or even prevented by addition of an appropriate low-valent dopant; (ii) phase separation is pronounced under oxidising conditions while under reducing conditions phase homogenisation is favoured [51,52]; (iii) sintering with decrease of surface area is very pronounced under reducing conditions, particularly when compared to oxidising ones [59]. These general comments clearly point out the critical need for further research aimed at a rationalisation of the role of the dopant in affecting thermal stability of the CeO_2–ZrO_2 mixed oxides, in order to develop new products for high temperature applications.

3.2.2. Oxygen storage of CeO_2–ZrO_2 mixed oxides

A remarkable property of the CeO_2–ZrO_2 mixed oxides compared to CeO_2 is their ability to easily remove bulk oxygen species at moderate temperature even in highly sintered samples. Thus the reduction peak at approximately 900 °C (Fig. 8, trace 1), which is associated with reduction of CeO_2 in the bulk shifts down to approximately 400 °C when a 40 mol% of ZrO_2 was inserted into the CeO_2 lattice to prepare a highly sintered $Rh/Ce_{0.6}Zr_{0.4}O_2$ mixed oxide catalyst [60]. This was associated with the ability of ZrO_2 to modify the oxygen sub-lattice in the CeO_2–ZrO_2 mixed oxides, generating defective structures and highly mobile oxygen atoms in the lattice which can be released even at moderate temperatures [61,62]. These early findings indicated that improved efficiency of the OSC property can be achieved by using CeO_2–ZrO_2 mixed oxides instead of CeO_2 since, even if the sample sinters under the high temperature reaction conditions, it should be more effective then CeO_2 due to the high oxygen mobility in the bulk; lattice oxygen species could effectively participate in redox processes even under fluctuating exhaust feed-stream conditions. It is now well recognised that when the OSC property is investigated by the TPR technique, no appreciable distinction between the reduction in the bulk and at the surface can be observed in the CeO_2–ZrO_2 mixed oxides. Both reduction at the surface and in the bulk proceed with similar energetics and occur at mild temperatures [63,64]. Typically, a single peak reduction profile centred around is 500 °C is obtained for a single phase CeO_2–ZrO_2 solid solution, the presence of multiple peaks being taken as an indication of presence of phase impurities [40]. However, the changes in the TPR behaviour are even more subtle because other factors such as textural properties and even the pre-treatment can affect the TPR profile [65–68]. For example, a combination of TPR followed by mild oxidation leads to reduction phenomena occurring at low temperatures [65], whereas when a high temperature (severe) oxidation is included as a pre-treatment, these low temperature processes reversibly shift to high temperatures [66,67]. There has been some debate as to whether migration of oxygen species in the bulk is limiting the rate of the reduction of the CeO_2–ZrO_2, or whether the kinetics of redox phenomena are rather dictated by surface properties [45]. However, recent findings confirmed the important role of the bulk properties for redox phenomena occurring at low temperatures [68,69].

As above indicated, the TPR technique has been routinely applied to investigate the redox properties of the CeO_2–ZrO_2 mixed oxides. It should be noted, however, that under real exhaust conditions, the λ value oscillates between the oxidising and reducing conditions with a frequency of about 1 Hz. In principle, this makes the so-called dynamic-OSC more useful compared to the TPR technique [12,71], since this technique allows detection of the oxygen available for redox processes on a time scale of seconds. In fact, it should be noted that even favourable TPR profiles, i.e. featuring reduction peaks at low temperatures, may not necessarily be associated with effective OSC due to occurrence of in situ deactivation phenomena on increasing the temperature of the measurement [72]. However, a very recent report suggested that correlation between TPR profiles and effective dynamic-OSC exists in that texturally stable samples featuring a TPR behaviour independent of the pre-treatment, e.g. a mild or severe oxidation, are those giving the stable and effective dynamic-OSC, minimising the deactivation phenomena [73]. This confirms the importance of the stabilisation of the textural properties in the CeO_2–ZrO_2 mixed oxides and the need for further improvement of the thermal stability compared to typical temperatures so far investigated (≈1000 °C).

3.3. Noble metals

Obviously, NMs represent the key component of the TWC, as the catalytic activity occurs at the noble metal centre. However, we purposely discuss the aspects related to the NM at this point, since its interaction with the various components of the washcoat critically affects the activity of the supported NM. In principle, the first aspect to be considered is the choice of the NM and its loading in the washcoat. Rh, Pd an Pt have long been employed in the TWCs and there is a general agreement about the specificity of Rh to promote NO dissociation, thus enhancing the NO removal [4,6,74,75], even if alternative mechanistic pathways for NO reduction have also been proposed [7,76,77]. Pt and Pd are considered as metal of choice to promote the oxidation reaction, even though Rh also has a good oxidation activity. In particular, besides some initial use in 1975–1976, Pd has extensively been added to TWC formulations starting from mid-1990s due to its ability to promote HC oxidation [10,11]. In fact, better A/F control [78] and modification of the support provided high NO_x conversion, comparable to the traditional Rh/Pt catalyst [79]. The increase of the use of Pd in the TWC technology adversely affected Pd market price, which is now comparable to that of Pt.

In fact, there is a large demand for Pd due to the fact that the straightforward way to increase the efficiency of the TWCs at low temperatures is that of increasing the NM loading, and particularly that of Pd, which for long was the cheapest NM among the three employed (Fig. 11). On the other hand, use of high NM loading may favour sintering at high temperatures, leading to deactivation of the TWCs, in addition to the fact that cost-effective TWCs are required by the market. In summary, the choice and loading of the NM is a compromise between the required efficiency of the converter and the market price of the NM; ideally a car maker would prefer to have available a choice of TWCs with different formulations, which would allow a selection to be made according to price fluctuations of the NMs.

3.4. Deactivation of the TWCs

Generally speaking, sintering of NM, leading to decrease of the number of active sites, is a major pathway for the deactivation of TWCs. In addition to sintering, poisoning of the catalyst may contribute to their deactivation. The latter phenomenon is essentially related to the mileage travelled, quality of the fuel and the engine lubricating oil [22]. However, there are a number of other routes which can contribute to deactivation of the TWCs: (i) sintering of the OSC promoter leading to loss of OSC and, possibly, to encapsulation of the NM [80]; (ii) sintering of Al_2O_3 and, more important, deactivation of Rh due to migration of Rh^{3+} into the alumina lattice [22]. The comprehension of the relative importance of the different deactivation phenomena is difficult due to the variability of the reaction conditions, TWC preparation methods, etc. For example, when NM are supported on CeO_2–ZrO_2 mixed oxides and aged at high temperatures under redox conditions, encapsulation of Pd and Rh within the pores of the support occurs, while it does not occur for Pt [81].

Although it has received relatively scarce consideration [82], the issue of sulphur poisoning of TWC needs some consideration. As above discussed, inclusion of CeO_2-based promoters into the washcoat

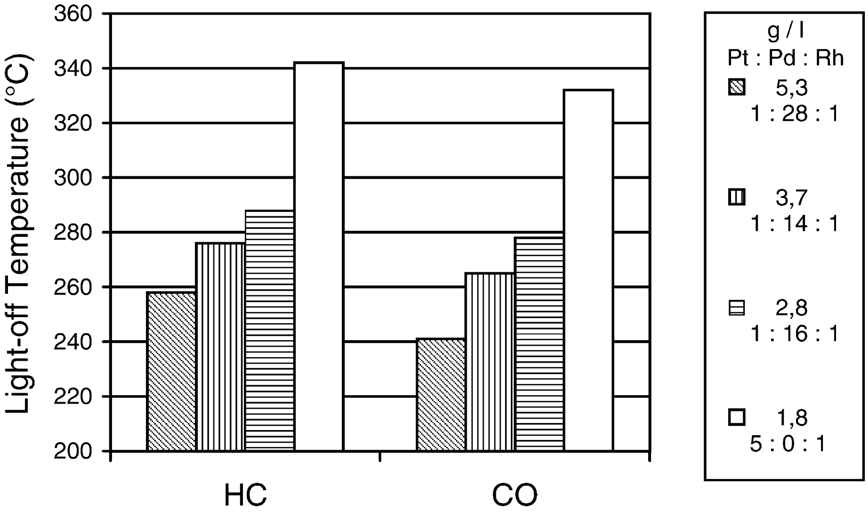

Fig. 11. Effect of NM loading on the light-off temperature in CCCs.

considerably enhances the conversion efficiency of the TWCs. On the other hand, both CeO_2 and ZrO_2 are known to easily adsorb SO_x species: sulphated ZrO_2 is a well-known solid acid catalyst [83], whereas CeO_2 is used as a $DeSO_x$ catalyst in cracking processes [84]. Investigation of reduced and oxidised CeO_2 revealed that SO_2 is adsorbed under various forms, with both surface and bulk-type of sulphates being observed [85,86], and it may even modify the microstructure of the CeO_2-based oxide [87]. Curiously, under oxidising conditions bulk sulphates decomposed by 600 °C, whereas surface sulphates persisted up to 700 °C [85]. Use of reducing conditions in the presence of H_2 favours elimination of sulphates as H_2S, which can be easily detected as rotten-egg odour [88], particularly in the presence of noble metal [89]. CO also promotes the reduction of sulphates to reduced oxy-sulphur species which unexpectedly increased the redox capability of the sulphated Pd/CeO_2 system compared to the sulphur-free analogue [90,91]. However, it was also observed that the OSC of CeO_2 is detrimentally affected by the presence of SO_2, while addition of ZrO_2 to CeO_2 increases the resistance of CeO_2 to sulphur poisoning, although more sulphur is adsorbed at the surface [82]. This may be associated with the generally higher OSC efficiency of the CeO_2–ZrO_2 mixed oxide compared to CeO_2 and the possibility that ZrO_2 acts as a sulphur scavenger. Ni containing oxides are sometimes added to the washcoat in the USA as sulphur scavengers, while their use in Europe is prohibited. In summary, adsorption of sulphur on the NM/CeO_2–ZrO_2-containing TWCs is rather complex and appears to be structure/adsorption conditions sensitive, which readily explains some contradictions in the literature. In terms of inhibition of the three-way activity it seems, however, that the issue of sulphur poisoning is much less stringent as compared, for example, to lean-$DeNO_x$ catalysts, due to the high temperatures achieved in the TWCs, which allow release of sulphur under driving conditions.

4. Future trends

4.1. Engine start-up emissions

As above discussed, TWCs represent a quite mature, highly effective technology for pollution abatement which, however, has some inherent limitations which need further improvement and development. These aspects are essentially related to: (i) low activity at low temperatures (start-up of the engine) and (ii) use of stoichiometric A/F. As far as the first aspect is concerned, it should be noted that roughly 50–80% of HC emissions during the test procedures are emitted before the TWC reaches the light-off temperature. When, in recent years, the emissions limits have been pushed down, it appeared clearly that minimisation of warm-up HC emissions was a major problem in automotive pollution abatement. This issue was been therefore addressed by introduction of the CCCs onto the market. This required development of TWCs featuring thermal stabilities well above 1000 °C [92].

In reality, the issue of the start-up emissions can be addressed by different approaches, some of which are listed in Fig. 12.

A first possibility is that of collecting the HC emitted during the warm-up of the converter in a HC trap, typically composed of hydrophobic zeolite. In an optimal trap, HC are trapped at low temperatures and as the temperature is increased above 250–300 °C, HC are released and converted on the TWCs [92]. A suitable trap must also feature very high thermal stability under hydrothermal conditions, which often is not the case for zeolite-based systems. We recall that temperatures as high as 850–900 °C may be reached in the under-floor catalysts. While such systems are still under investigation, alternative approaches have been indicated [92,93]. It must be recognised that to minimise the emissions, the catalysts must be heated-up in a minimum time. This can be achieved, for example, by electrically (Fig. 12) or combustion/chemically heated catalysts. In the latter case hydrogen and oxygen, or CO-rich feed is flowed over the catalysts [93]. Oxidation of both CO and H_2 are easy and exothermic reactions, which occur at low temperatures over the TWCs [94], leading to rapid heating of the catalyst. However, storage of H_2 on the vehicle or use of rich A/F which generates high CO and H_2 emissions, brings complexity to the de-pollution system. Large amounts of HC are in fact emitted at rich A/F, which require an additional HC trap.

Use of complex technology clearly pushes-up costs while the simplest technology is desirable. Accordingly, there has been a strong effort aimed at improving the thermal stability of the washcoat [42]. With

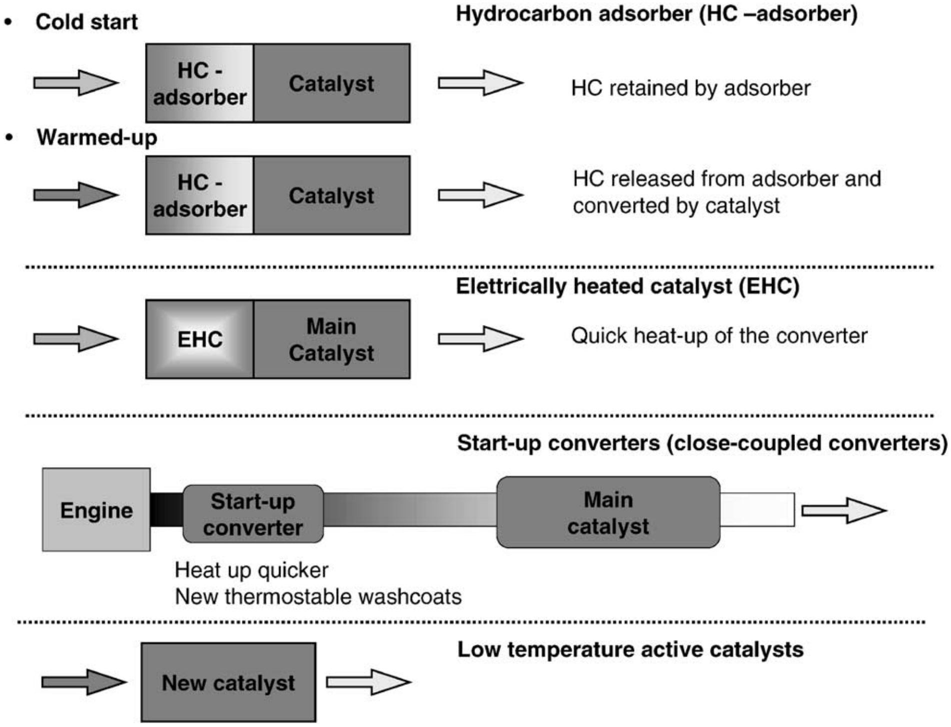

Fig. 12. Some strategies for the abatement of engine start-up emissions.

the availability of thermally stable washcoats, application of a start-up converter, i.e. converter that is closely coupled to the exhaust manifold, became feasible. This converter allows extremely rapid heating of the catalyst, leading to enhanced conversions during the warm-up of the engine. Metallic converter can be easily shaped into the exhaust manifold and are very convenient for such application also due to their low heat capacity. In general, the composition of the CCC is related to that of the typical TWC in that NM metals and particularly Pd are employed to promote HC conversion. The OSC promoter may be omitted from these formulations since it promotes CO conversion, leading to local overheating because of this highly exothermic reaction [92]. On the other hand, for the purpose of the OBD II technology, there is a necessity to monitor the OSC efficiency from the start-up of the engine. Accordingly, ZrO_2–rich doped CeO_2 promoters with very high thermal stabilities [42,73,95], are often added to this catalyst.

An alternative approach is that of developing new catalysts showing high conversion efficiency at low, nearly ambient, temperature [93]. A large part of these investigations have been triggered by the observation by Haruta et al. [96,97] that gold catalysts are able to efficiently oxidise CO even at subambient temperature provided that nano-dispersed Au particles are prepared on the support. Thus, light-off temperatures in the conversion of the exhausts as low as 100 °C could be achieved by depositing small Au particles on reducible oxides such as CeO_2 and TiO_2 [98]. However, the durability of gold catalysts under harsh conditions is still an issue, significant deactivation of cobalt oxide promoted Au catalysts was observed already after 157 h of reaction at 500 °C under simulated exhaust [99]. There is in fact a flourishing activity in the field of low temperatures catalysts [97,100,101], other noble metals, in addition to Au, being effective in low temperature oxidation reactions, provided that appropriate synthesis methodology is employed [100]. To our knowledge, however, due to the nano-dispersed nature of these catalysts, the issue of thermal stability, even at moderately high temperatures has not been solved as yet. Supported metal nano-particles are, in fact, quite mobile on the surface, even at ambient temperature in the case of gold [101], which makes prevention of sintering phenomena difficult. We believe that thermal stabilisation of nano-dispersed metals may represent a new breakthrough point in the development of these environmental catalysts.

4.2. Lean DeNO$_x$ catalysts

The recently approved California legislation on automobile fuel consumption has prompted the necessity of developing new and more effective catalysts capable of removing NO$_x$ even in excess of O_2. As indicated in Section 2, lean-burn gasoline and diesel engines, due to the high A/F used in the combustion process, can achieve significant fuel savings, however, under these conditions no TWC is effective in reducing NO$_x$ due to the excess of O_2, which is competing for the reducing agent, in particular CO.

Studies on NO$_x$ removal under oxidising conditions were triggered by the discovery in 1991 that HCs could act as selective reducing agents under excess of O_2 [102]. This discovery was followed by a feverish activity in the field of lean-DeNO$_x$ and more then 50 catalysts were reported in 1991–1992 [103]. Since then this topic has been reviewed by several researchers, even though a comprehensive knowledge of the exhaust lean technology is still missing [2,5,102–116]. As outlined in a report issued by MECA (Manufacturers of Emissions Controls Association) [117] there are two major strategies to control the NO$_x$ emissions under oxidising conditions:

- DeNO$_x$ (lean-DeNO$_x$) catalysts;
- NO$_x$ adsorbers (NO$_x$ traps).

The former strategy employs a direct NO$_x$ reduction catalyst, usually consisting of Pt/Al_2O_3 and a metal-loaded zeolite for NO$_x$ reduction at, respectively, low and high temperature. The NO$_x$ adsorber technology is sometimes called a NO$_x$ storage/reduction (NSR) catalyst. In this case typically a Pt/BaO/Al_2O_3 catalyst is used to store NO$_x$ under oxidising conditions as adsorbed “nitrate” species, which are then released and reduced on a traditional TWC by temporarily running the engine under rich conditions. Let us now examine in some detail these systems.

4.2.1. Pt/Al_2O_3 and derived systems

The activity of Pt/Al_2O_3 catalysts for NO$_x$ reduction under lean exhaust conditions has been investigated in detail by Burch et al. [118–136]. They extensively analysed the effects of the nature of the noble metal, reducing agent, sulphur addition, nature of additives and of the support, and reaction mechanism.

A typical reaction profile for HC reduction over Pt/Al_2O_3 is reported in Fig. 13. This figure summarises some general features of Pt/Al_2O_3 lean-burn catalysts, that is: (i) a maximum of NO conversion at relatively low temperature, NO$_x$ conversion peaking as the HC conversion reaches 100% in the case of C_3H_6; (ii) comparable starting temperatures for the NO reduction and HC oxidation; (iii) significant NO_2 formation at high temperatures when all the HC is burned-out; (iv) strong sensitivity of the NO conversion to the nature of the reducing agent (saturated vs. unsaturated HC); (v) poor selectivity towards di-nitrogen formation of the Pt catalyst, N_2O being the major product at low temperatures. As stated at point (iv), this general behaviour strongly depends on

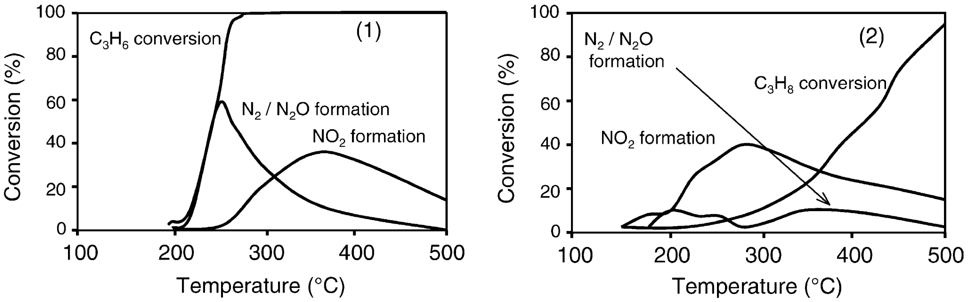

Fig. 13. Typical light-off behaviour for: (1) C_3H_6–NO–O_2 and (2) C_3H_8–NO–O_2 reactions over Pt/Al_2O_3. Pt: 1 wt.%, reactant feed: 1000 ppm C_3H_x, 500 ppm NO, 5% O_2. $W/F = 4 \times 10^{-4}\,g\,min\,ml^{-1}$ (GHSV 72,000 h^{-1}) (after Ref. [121]).

the nature of the reducing agent: non-reactive (short chain-saturated) HCs behave somewhat differently from reactive HCs such as alkenes or long-chain HC [127].

Let us discuss some important aspects of the above quoted properties of the Pt lean-DeNO$_x$ catalysts.

4.2.1.1. Light-off behaviour of the Pt catalysts. NO conversion typically shows a volcano shaped curve irrespective of the nature of the HC. This is due on one hand to the fact that NO$_x$ always initiates together with the HC oxidation and on the other hand to the fact that, with few exceptions, the maximum NO conversion corresponds to 100% HC conversion. At higher temperatures, when all the HC is consumed, significant NO_2 formation occurs by reaction of NO with excess O_2, the amount of NO_2 formed being limited by thermodynamic constrains. Note, however, that NO_2 concentration that apparently exceeded thermodynamic values were also reported for an Ag/Al_2O_3 system [137]. This fact was attributed to the presence organo-nitrite species as intermediates of the SCR process, which oxidation/decomposition led to NO_2 production.

The maximum of the NO$_x$ conversion is obviously affected by the space velocity (SV/GHSV). For a typical light-off curve, the reaction rate is kinetically limited only below the light-off temperature, while above light-off the reaction rate is limited either by heat or mass transfer. As a consequence, the maximum of the NO$_x$ conversion moves to low temperature and its intensity increases as SV decreases, however, this effect is not directly proportional to the decrease of the SV. Thus the maximum of the NO reduction peak moved from 200 °C (conversion 70%) to 215 °C (conversion 47%) as the SV was increased from 10,000 to 50,000 h^{-1}, while at intermediate SV = 25,000 h^{-1} a conversion of 57% was observed at approximately 210 °C [16]. From a practical point of view, exhaust emissions of a diesel engine were characterised by SV = 28,000–88,000 h^{-1} as the temperatures varied between 160 and 400 °C during the MVEuro2 driving cycle [16].

A corollary of this fact is that any comparison of activities simply based on light-off activities may be strongly misleading. Differences in light-off temperatures are in fact related to the number of active sites (Pt_s), total flow-rate (F) and kinetic law for the reaction by the following equation [138,139]:

$$\frac{1}{T_2} - \frac{1}{T_1} = \left(\frac{R}{E_a}\right) \ln \frac{f_2(c)\, \mathrm{Pt_s}\, F_2}{f_1(c)\, \mathrm{Pt_s}\, F_1} \qquad (1)$$

For Eq. (1), a rate equation of the type $r = k(T) f(c)$ is assumed, where $k(T)$ is the rate constant for NO conversion, which depends on the temperature; and $f(c)$ represents the remaining factor of the rate equation, which depends on surface coverage and is independent of temperature [138,139]. An inspection of Eq. (1) reveals that upon comparison of the activities of two catalysts with different dispersions (i.e., there are two different Pt_s terms) under equivalent reaction conditions (i.e., $F_1 = F_2$ and $f_1(c) = f_2(c)$), the higher the number of active sites the lower the light-off temperature. This means that the specific activity of two catalysts may be compared using the light-off behaviour only when an equal number of active sites is employed in the experiment. Unfortunately, very few investigations concerning lean-DeNO$_x$ have reported reaction rates, light-off temperature being generally shown, which makes direct comparison difficult. Note that when long-chain HC are investigated, which can easily generate coke at the catalysts surface, the light-off behaviour may not be relevant to the true catalytic activity as pseudo-steady states were observed below light-off temperature for short to medium periods (0.1–2 h) followed by a deactivation of the catalyst [131]. It is important to keep present these limitations when activity from different sources is compared.

Reaction rates and kinetic law for $C_3H_6/NO/O_2$ reaction were reported in the literature for Pt/Al_2O_3 and Rh/Al_2O_3 [140,141]. For Pt/Al_2O_3 the following expression were found experimentally at 230–236 °C (NO and C_3H_6 250–4000 ppm, O_2 0.5–12%, W/F = 0.0018 g s ml^{-1}, GHSV ≈ 100,000 h^{-1}, apparent activation energy 24±3 kcal mol^{-1}):

$$\text{reduction}: \quad r(\mathrm{NO}) = k_{\mathrm{red}} \frac{[\mathrm{O_2}]}{[\mathrm{C_3H_6}]^{0.5}}$$

$$\text{oxidation}: \quad r(\mathrm{C_3H_6}) = k_{\mathrm{ox}} \frac{[\mathrm{O_2}]}{[\mathrm{NO}]^{0.5}[\mathrm{C_3H_6}]^{0.5}}$$

For comparison, the kinetic expression for the combustion of C_3H_6 measured at 158 °C was

$$\text{combustion}: \quad r(\mathrm{C_3H_6}) = k_{\mathrm{comb}} \frac{[\mathrm{O_2}]}{[\mathrm{C_3H_6}]^{0.5}}$$

The apparent activation energies for NO reduction and C_3H_6 oxidation were measured as 22 and 24 kcal mol^{-1} over Pt (1.5 wt.%)/Al_2O_3 [141]. Interestingly, NO_x, even if present at ppm level, interferes with the HC oxidation. We recall that modification of CO oxidation kinetics in the presence of NO is typically assumed as a direct indication that NO removal occurs through the NO/CO reaction over TWCs [4]. In summary, independently of the reaction mechanism, the key factors in the light-off behaviour of Pt lean-DeNO$_x$ catalysts is that a narrow maximum of activity is observed around 270–300 °C. The width and position of this maximum of activity depends on the reaction conditions and nature of the catalyst. As is shown below, also the nature of the HC also plays a fundamental role in the volcano shaped NO_x conversion curve because of the different HC reactivity.

4.2.1.2. The effect of the reducing agent and promoters on the reaction mechanism. The effect of the nature of the reducing agent was investigated in detail by researchers from Degussa (OMG) [142]. Even though the nature of the catalyst employed was not specified, except that a 50 g/ft^3 Pt honeycomb catalyst was used, the finding of this paper represent typical results observed over Pt/Al_2O_3 in subsequent papers. These findings can be summarised as follows:

- There is a remarkable difference in the response of the Pt catalyst to the nature of the HC reducing agent, e.g. the temperature of the maximum of HC and NO conversion is nearly independent of the type of linear alkene, while an increase of the length of the chain of the alkane significantly shifts down this temperature.
- At comparable HC chain length saturated HC are much less effective compared to unsaturated ones. Remarkably $C_{16}H_{34}$, which is a typical diesel fuel component, featured an activity comparable to that of C_3H_6.
- Use of alcohols resulted in high activity at low temperatures, the nature of the alcohol affecting the activity to a lesser extent compared to alkanes.
- Use of aromatic compounds as reducing agent showed a strong dependence of the conversion efficiency on the reactivity of the molecule.

The remarkable difference of the catalytic behaviour between the saturated and unsaturated HCs was rationalised in terms of the different reaction pathway for the NO reduction in the presence of either saturated or unsaturated HC (Fig. 14) [121,125]. It appears that reduction of the unsaturated HC can be depicted as a NO_x dissociation reaction occurring the metal centre, where the unsaturated HC is responsible for the removal of the adsorbed oxygen generated by the NO_x dissociation. In the presence of weakly adsorbed reducing agent, such as C_3H_8, adsorbed atomic oxygen is the dominant species on the metal surface under reaction conditions. The C_3H_8 oxidation is inhibited by both O_2 and in the facile oxidation of NO to NO_2. It is believed that the rate determining step in C_3H_8 oxidation by O_2 is the dissociative chemisorption of C_3H_8 involving the breaking of a C–H bond [123,125]. This is a difficult reaction and strongly depends on the nature of the HC, which accounts for the strong

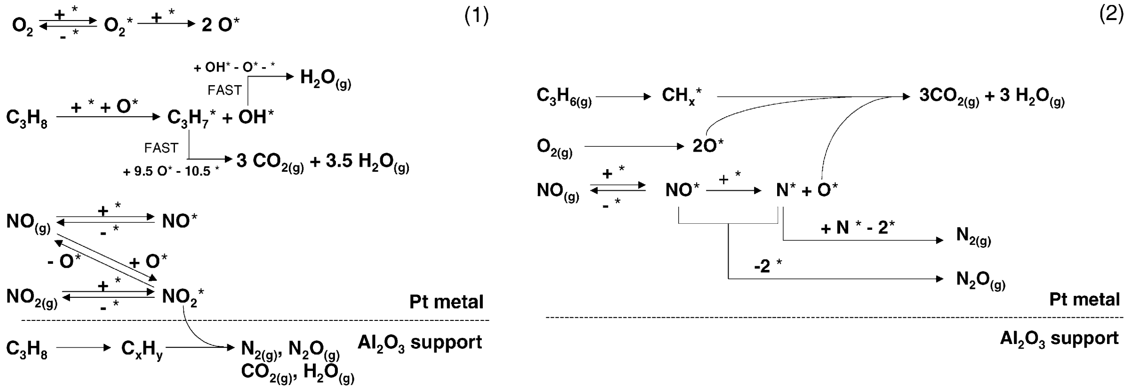

Fig. 14. Proposed reaction mechanism for lean-DeNO$_x$ reaction over Pt/Al_2O_3 for alkane (1) and alkene (2) conversion (after Ref. [121]).

effect of the carbon chain length upon the DeNO$_x$ activity.

In addition, a comparison of different Pt/Al$_2$O$_3$ catalysts promoted by metal oxides (Ba, Ce, Co, Cs, Cu, K, La, Mg, Mo, Ti) or noble metals (Ag, Au, Pd, Rh) in the lean NO$_x$ reaction, using C$_3$H$_6$ as a reducing agent, showed that even if the promoters have a significant effect (beneficial or otherwise) on the activity and temperature range of operation of Pt/Al$_2$O$_3$, they have no significant effect on the N$_2$/N$_2$O selectivity. The similarity in behaviour of the promoted catalysts and unpromoted Pt/Al$_2$O$_3$ suggests that the reaction mechanism was similar for all the catalysts tested [124]. The ability of the Al$_2$O$_3$ support to promote the interaction of the adsorbed/migrated NO$_x$/C$_x$H$_y$ species generated from saturated HC, seems a particular property of this support, since changing the support to SiO$_2$ resulted in almost no reaction even with comparable Pt loading and dispersion. Finally, a comparison of different HCs as reducing agent revealed an unusual ability of aromatic HC (toluene) to promote high selectivity of the Pt catalysts towards formation of N$_2$ [122]. It should be also noted that when long-chain HCs are employed, the light-off activity may be very different from steady-state activity in that below or close to light-off temperature (generally chosen as 50% of conversion), catalysts poisoning with time-on-stream was observed [127]. By increasing the reaction temperature conversion of adsorbed carbonaceous species occurred, thus recovering the catalyst activity [130]. No deactivation was observed with small HC, formation of carbonaceous species being minimal in this case.

The effect of addition of SO$_2$ to the reaction feed appears in line with the above interpretation of the effect of the HC in that strong poisoning of activity was observed when C$_3$H$_8$ was employed as reducing agent due to the formation of aluminium sulphate. This is responsible for the poisoning of the catalytic sites at the support [128]. In contrast the activity was much less affected in the case of C$_3$H$_6$, which is in line with the smaller sensitivity of the Pt particles towards sulphur poisoning compared to the support.

Even though this reaction mechanism was questioned, in particular due to the lack of XPS evidence for reduced Pt sites [143], we believe that the major findings and suggestions reported by Burch and co-workers still provide an important guide-line for development of a new generation catalyst. In fact, despite the intensive research in the literature, the effect of the nature of the support has little been investigated [124,126,143–145], and most of the studies were carried out using C$_3$H$_6$ as reducing agent, where little or no effect of the support should be expected. In fact, we believe that in this case the major role of the support is to affect the Pt dispersion rather then other effects, thus modifying the activity of the supported metal. When saturated HCs are included in the feed, effects of support composition were detected [143], however, there is not enough evidence on a clear effect of the different supports in promoting Pt activity in lean-DeNO$_x$.

4.2.2. *Other lean-DeNO$_x$ catalysts*

Numerous other catalytic systems have been investigated as DeNO$_x$ catalysts, however, they appear much less applicability as next generation catalyst due to generally low activity and/or stability of such systems. For sake of convenience we will group all the catalysts in the following categories:

- Cu-ZSM5 and related systems;
- metal oxide catalysts.

As above written, Cu-ZSM5 represented the first major candidate for lean-DeNO$_x$ catalysts, even though it was quickly recognised that several problems affect the Cu-zeolite catalysts [103]. These include: (i) poor hydrothermal stability of Cu species and zeolite framework; (ii) appreciable activity only at high temperature (300–400 °C), which only allows the use of such system in conjunction with NM low temperature catalysts; (iii) generally poor activity under real exhaust and at high space velocities. The higher range of reaction temperatures compared to Pt catalysts makes these systems of potential interest for lean-burn gasoline engine, where such high temperatures are more easily met compared to the diesel engine.

With the aim of improving the thermal stability of the zeolite catalysts, a variety of supported and even unsupported metal oxides have been investigated. ZrO$_2$ itself was chosen as a possible candidate. Cu/ZrO$_2$ and other supported metal oxides, both sulphated and sulphur-free, have been investigated to some extent with the aim of improving the thermal stability of the catalyst compared to the zeolitic system [146–154]. Even though some interesting activities were claimed, to our knowledge, there is not sufficient evidence for possible application of such systems under real exhaust conditions. In fact, even though some increase of thermal/hydrothermal stability could be achieved, the activity is generally poorer compared to the Cu-ZSM5 system. As a general comment, it seems that despite the Edisonian type of research on different metal oxides as $DeNO_x$ catalysts, the "high activities" sometimes claimed by the authors, withstand with difficulties the harsh exhaust conditions. A relatively recent comparative study of several types of "promising" lean-$DeNO_x$ catalysts under diesel conditions is very illustrative in this respect [155]: after testing nine different classes of catalysts (Pt/Al_2O_3, Rh/Al_2O_3, Ag/Al_2O_3, Pt-ZSM5, Cu-ZSM5, Pt/In-ZSM5, CeZSM5+Mn_2O_3, Co/Al_2O_3, and $Au/Al_2O_3 + Mn_2O_3$), the authors came to the conclusion that despite the fact that some high activities could be measured, particularly on the NM-containing catalysts, there is no single phase catalyst capable of satisfying the practical demand for NO_x removal from diesel exhaust.

Ag catalysts are also among those extensively studied since high activity were reported, particularly when alcohols are employed as reducing agents (see, for example [137,155–165]). A general comment concerning the Ag based catalysts is that, due to the low melting point of Ag, extensive sintering of the catalyst may be expected even at relatively low temperatures. The catalytic activity was shown to depend on the Ag particle size [166], high particle sizes favouring the unselective HC oxidation and N_2O formation at low temperatures (Fig. 15). On the contrary, highly dispersed Ag particles favour formation of N_2 but the reaction occurs at higher temperatures. This was explained by the different reaction pathway according to the nature of the supported Ag phase (Fig. 16).

The high sinterability of Ag may represent an important drawback for practical application unless particular synthesis methodology is employed [167,168]. As shown in Fig. 15, high activity and N_2 selectivity of the Ag catalysts is observed in the "high" range of temperatures; accordingly this catalyst may be considered as a substitute for the Cu-ZSM5 component in a full-range of temperatures operating lean-$DeNO_x$ catalyst [2,169]. To promote the activity at low temperatures, Ag could in principle be sintered, however this promotes the unselective HC oxidation [166]. An interesting way to promote the activity of these catalysts is to add another NM to the system [170,171].

Recently, we have shown that use of ZrO_2 or ZrO_2-rich CeO_2–ZrO_2 mixed oxides as supports for Ag strongly improves the activity at low temperatures (Fig. 17) [172]. As shown by comparison of activities of catalysts with different Ag dispersion

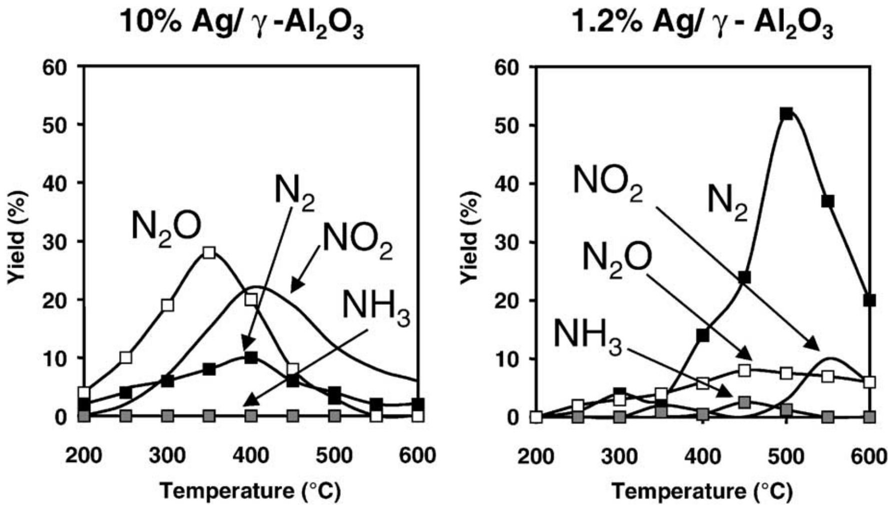

Fig. 15. Effect of Ag loading on the activity and product selectivity in Ag/Al_2O_3 catalysts (after Ref. [137]).

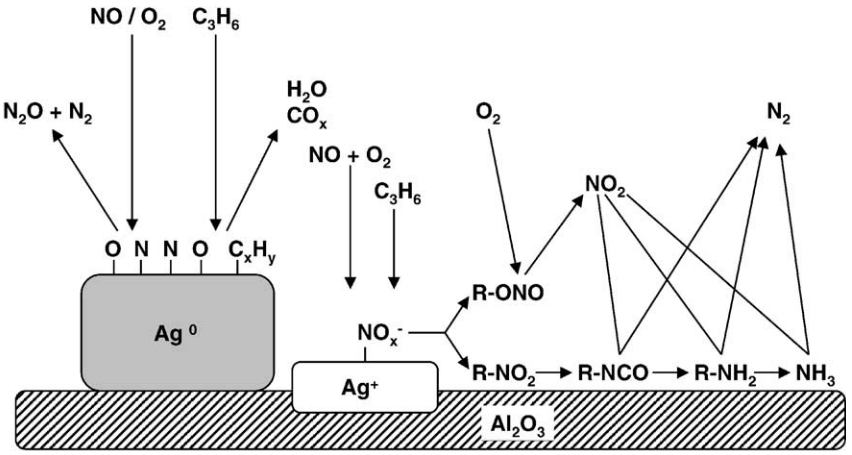

Fig. 16. Reaction mechanism(s) proposed for the lean-DeNO$_x$ reaction over Ag/Al$_2$O$_3$ catalysts (after Ref. [137]).

[172], the activity of Ag invariably occurs at lower temperatures on ZrO$_2$-containing supports compared to Al$_2$O$_3$ supports. More important is that the use of ZrO$_2$-containing supports remarkably facilitates the regeneration of the catalysts from SO$_x$ poisoning compared to Ag/Al$_2$O$_3$.

4.2.3. Bi-functional lean-DeNO$_x$ catalysts

The idea of bi-functionality to improve the activity of the lean-DeNO$_x$ catalysts has been pioneered by Misono and co-workers. These studies were recently reviewed [173], accordingly we refer the reader to this review. Of the several systems described, it is important to focus the mechanistic features of the authors' work. Essentially, the authors favour the reaction pathway which proceeds with formation of NO$_2$ as reaction intermediate, which then efficiently reacts with adsorbed HC to give surface intermediates. These intermediates then decompose leading to an overall reduction of NO$_x$. A redox type component such as Mn$_2$O$_3$ or SnO$_2$ is also added, which favours oxidation of NO to NO$_2$ (Fig. 18).

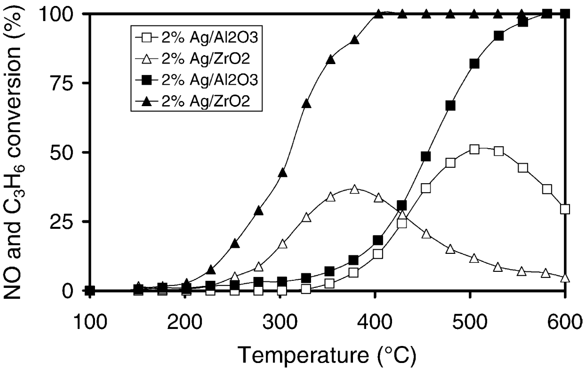

Fig. 17. Effect of the nature of the support on lean-DeNO$_x$ activity of Ag catalysts: NO$_x$ reduction (empty symbols), C$_3$H$_6$ oxidation (filled symbols). The 1000 ppm C$_3$H$_6$, 1000 ppm NO, 5% O$_2$, W/F = 0.05 g s ml^{-1} (after Ref. [172]).

An interesting aspect of these systems is that the presence of water, which normally deactivates the DeNO$_x$ catalysts, can even improve the catalytic activity (Fig. 19). This was attributed to the partial suppression of the direct HC oxidation at Mn$_2$O$_3$ (Fig. 18) that is responsible for non-selective HC oxidation.

Among the bi-functional systems, the NM/zeolite catalysts, containing particularly H-ZSM5, should also be quoted. A number of researchers have indeed employed both Pt/ZSM5 and Pd/ZSM5 as bi-functional systems for the lean-DeNO$_x$ (see, for example [147,173–180]). Typically, such catalysts and particularly those Pd-based were employed for lean-DeNO$_x$ using CH$_4$ as reducing agent. The bi-functionality of this type of catalyst is related to the necessity of acid sites, which apparently allow activation of the HC at the support leading to selective NO$_x$ reduction. In fact, using Na-ZSM5 as a support, no NO$_x$ reduction was detected. Several zeolites were employed for the CH$_4$/NO/O$_2$ reaction, however,

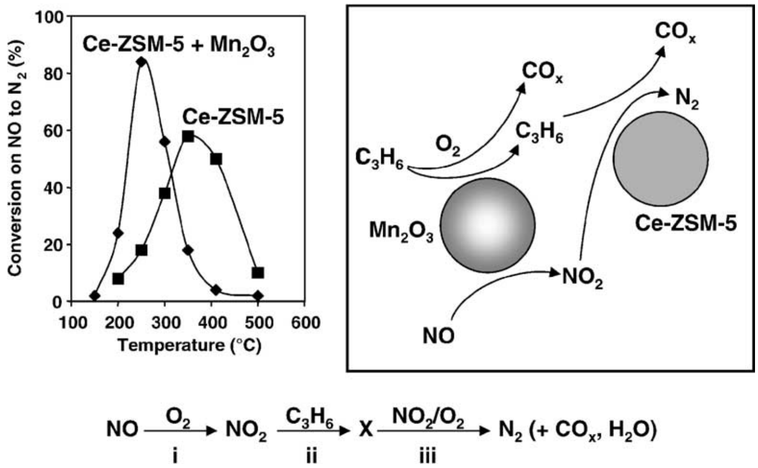

Fig. 18. Effect of addition of Mn_2O_3 (as physical mixture) on the DeNO$_x$ activity of Ce-ZSM5; and the proposed reaction mechanism (after Ref. [173]).

significant deactivation of the catalyst occurred in the presence of water and SO$_x$.

While a somewhat extensive description of the various attempts to develop efficient lean-DeNO$_x$ catalysts is reported here, it is important to outline that these systems do not ensure sufficient activity to foresee practical applications in a future. Development of new breakthrough strategies is an important target for the comming years to achieve significant environmental benefits from the use of lean, high-efficiency engines.

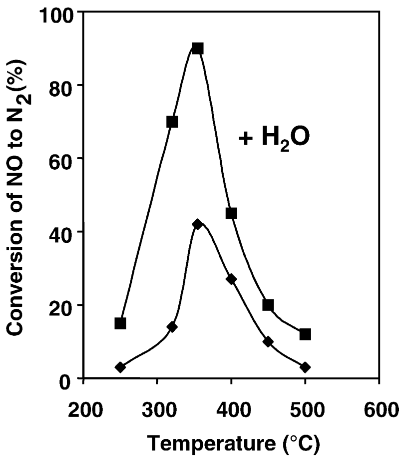

Fig. 19. Effect of addition of H_2O on the activity of Mn_2O_3/Sn-ZSM5 bi-functional catalyst (after Ref. [173]).

4.3. Lean NO$_x$ traps

The discovery by Toyota researchers of the so-called NSR catalysts also triggered feverish activity in lean-DeNO$_x$ studies [181–183]. The principle of the reaction mechanism of these systems appears well established [183]. Under oxidising conditions NO$_x$ are stored at the surface of a Ba-containing catalyst under various forms (surface nitrites/nitrates), which exact nature is still matter of debate [184–187] (Fig. 20). After a certain period, which length is an important factor and is correlated to the specific emission/catalyst characteristics, the A/F ratio is set to rich and the stored NO$_x$ species are reduced over Pt or, more generally, TWC-type catalyst to N_2 [183].

The mechanism of NO$_x$ adsorption and desorption/reduction has been investigated by a number of authors [112,184,185,187–197]. It appears now clearly the storage/reduction is rather complex process due to the complex nature of the exhaust mixture. For example, model studies performed on Pt/BaO/Al_2O_3 suggested that the first step is the oxidation of NO to NO_2, which is active species being adsorbed on the surface [190,191], even though kinetic studies could not distinguish whether surfaces nitrites are formed first and then oxidised to nitrates or whether both species are formed directly by a disproportionation mechanism [194]. However, the final species that is strongly held on the surface and accounts for the majority of NO$_x$

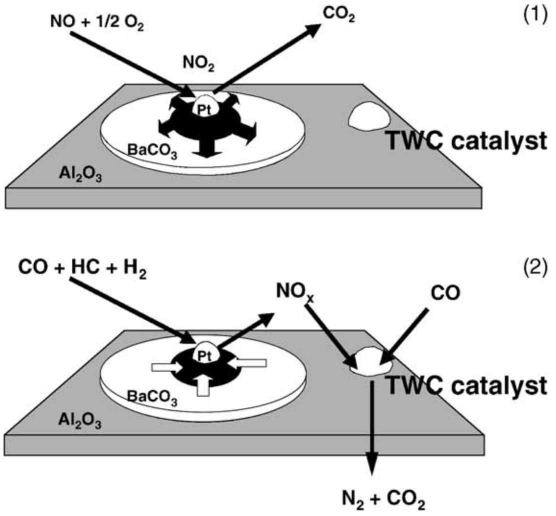

Fig. 20. Principle of operation of an NSR catalyst: NO_x are stored under oxidising conditions (1) and then reduced on a TWC when the A/F is temporarily switched to rich conditions (2).

stored appears to be a nitrate species, in particular at high temperature due to the low thermal stability of nitrite. Whatever is the true mechanism, it must be underlined that the kinetics and the extent of storage are heavily affected by the presence of water and CO_2 in the exhausts: CO_2 slows down the NO_x adsorption kinetics as the reaction can more appropriately be seen as a transformation of surface carbonates into nitrates, e.g. CO_2 strongly competes with NO_x for the adsorption sites [190,196]. This competition, on the other hand, increases the rate of NO_x releases under the rich-spike [188,189]. The effect of water is more controversial in that promotion of NO_x adsorption was observed below 250 °C by addition of small amounts of water (1%), whereas at higher temperature an inhibition effect was observed [194]. However, such promoting effect was not seen when both water CO_2 were co-fed.

The NSR technology is by far the most reliable and attractive lean-DeNO_x technology and it has been commercialised in Japan where low sulphur gasoline is available. In fact, the major drawback of the NSR catalyst is its sensitivity to SO_x due to the fact that surface sulphates are invariably more thermally stable compared to the nitrates [198]. The durability aspects of the NSR catalysts were addressed, for example, by researchers from OMG [199] and there seems to be general agreement that poisoning of the NO_x storage function is directly related to the amount of SO_2 passed over the catalyst. This is an important aspect since it suggests that for application of these catalysts to US or European markets, where higher sulphur contents are present in the fuel compared to Japan, appropriate strategies to develop sulphur resistant NO_x trap must be applied. In addition to the obvious requirement of lowering of sulphur content in the fuel, there are strategies that can be adopted for increasing sulphur tolerance of the converter: (i) adoption of an SO_x adsorber that protects the NO_x trap and is periodically regenerated; (ii) modification of the catalyst composition to promote of the removal efficiency of the adsorbed SO_x. An interesting example of such strategies was recently reported by Toyota [200,201]. In their system, TiO_2 was added to protect the barium-based trap from sulphur poisoning due to its high sulphur tolerance. LiO was added as it was observed that Li-promoted Al_2O_3 releases accumulated sulphur more easily compared to pure Al_2O_3. Rh/ZrO_2 was also employed to enhance the sulphur removal under reducing conditions due to its effectiveness as a steam reforming catalyst. In fact, an efficient H_2 generation under the rich-spike of the cycle strongly favours the removal of adsorbed SO_x. It should be noted that release of H_2S from the catalysts is undesirable, accordingly special schedules of the modulation of the A/F during the rich phases can be adopted, which pump additional oxygen during the rich-de-sulphation phase minimising H_2S release [202]. Finally, thermal deactivation due to sintering of the barium species and formation of barium aluminates may represent an issue in terms of durability of the catalyst [203]. Accordingly, thermally stable Ba-containing materials, such as doped aluminas or perovskites, has been investigated as NO_x absorbers [184,185,204].

It is worth of noting that the NSR strategy has also been applied to diesel engines. In this case generation of the rich conditions must be carefully considered as switching A/F to rich conditions easily generates typical black-smoke-containing emissions, often found in older vehicles. Low temperature smokeless combustion with a massive EGR or, more frequently, post-injection of fuel are employed to temporarily generate rich exhaust. The interesting point is that the NSR component may be deposited on the walls of the porous ceramic filter so that the precious metal can

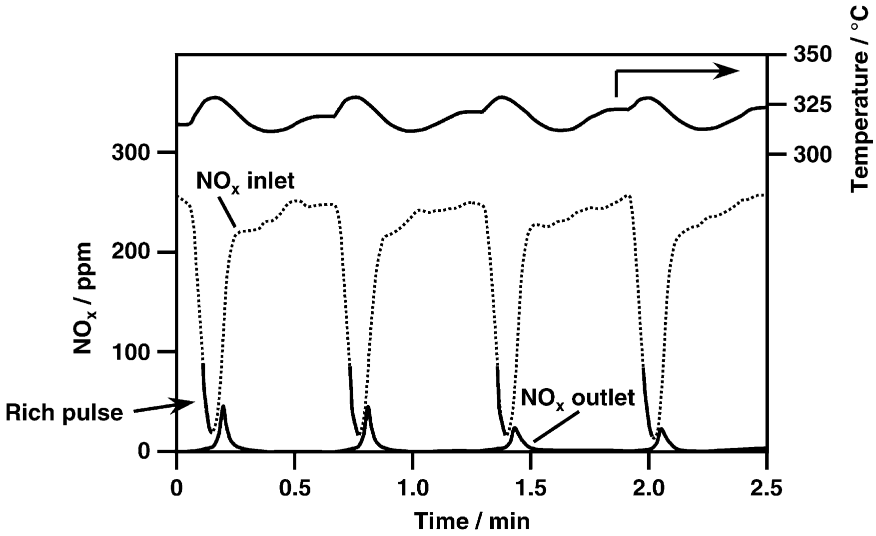

Fig. 21. Engine-out and tailpipe-out emissions from a 1.9 L diesel engine over an NSR catalysts deposited on a ceramic filter. Notice that similar efficiencies may be achieved over the NSR catalysts in the lean gasoline engines (after Ref. [205]).

contemporarily promote removal of the particulate [205]. Thus, very high pollutant conversion efficiency (ca. 80%) could be obtained in the engine test procedure (Fig. 21). Clearly, the issue of trap deactivation becomes even more stringent in the case of diesel vehicles due to the generally higher amounts of sulphur in the fuel and low operating temperatures that do not allow efficient trap regeneration. Rich conditions for several minutes and temperatures as high as 650–700 °C are typically needed to achieve effective trap de-sulphurisation [202].

4.4. Selective catalytic NO_x reduction using urea

Due to the limited success of HCs as efficient reducing agent under lean conditions, the use of urea as an alternative reducing agent for NO_x from heavy duty diesel[2] vehicles has received attention. Selective catalytic reduction of NO_x with NH_3 in the presence of excess O_2 is a well implemented technology for NO_x abatement from stationary sources [206]. Typically, vanadia supported on TiO_2, with different promoters (WO_3 and MoO_3) are employed in monolith type of catalysts. A sketch of an arrangement for the urea based NO_x abatement technology is shown in Fig. 22. Typically, the urea solution is vaporised and injected into a pre-heated zone where hydrolysis occurs according to the reaction:

$$H_2N\text{–}CO\text{–}NH_2 + H_2O \rightarrow CO_2 + 2NH_3$$

Ammonia then reacts with NO and NO_2 on the reduction catalyst via the following reactions:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

This approach has proved to be quite successful and high NO_x (up to 80%) could be achieved on HD under driving conditions, even after reasonably high mileages (200,000–300,000 km), the activity decreased to about 75–80% of the initial value after over 500,000 km [207,208]. A major problem of such system is that extreme care must be exercised to develop a suitable urea injection strategy that avoids overloading of the system leading to ammonia slip [209].

---

[2] Light-duty (LD) diesel engines are generally defined as vehicles with an engine displacement of less than 4 l and power output of up to 100 kW, and are characterised by relatively high engine speeds. LD engines would normally be found in passenger vehicle and light commercial vehicle applications. Heavy duty (HD) diesel engines may be generally defined as of displacement greater than 8 l and power outputs of greater than 150 kW. HD engines are found in heavy road transport, industrial and marine applications. Medium duty engines fill the gap in the middle and are found in medium size trucks, buses and light industrial equipment.

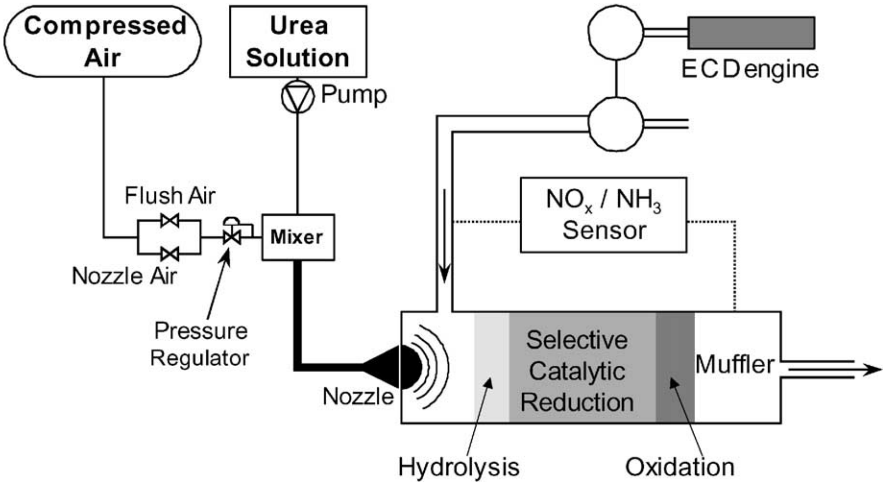

Fig. 22. A typical arrangement for abatement of NO_x from a heavy duty diesel engine using urea as reducing agent.

Typically, ammonia slip should not exceed 10 ppm. While the efficiency of urea-SCR technology is recognised [210], there are certainly still a number of issues concerning the catalyst efficiency at low temperatures, the design of compact converter systems that require higher conversion efficiency and, last but not least, the issue of generalised urea distribution when fuelling the vehicle.

Given the efficiency of such systems, the application of the urea-SCR technology to LD vehicles was also investigated [211]: while appreciable NO_x can be achieved, it must be recognised that a ratio of engine displacement-to-catalyst volume of 1:3 is typically employed for the urea-SCR systems that may represent a serious problem in compact LD vehicles. Clearly, an important improvement of the catalytic performances is needed before such systems can be effectively considered for LDV application.

4.5. *Particulate matter removal*

Even though this topic is specifically related to diesel engines, the general interest of these systems is related to the above quoted desire to use high-efficiency engines. Diesel particulate matter (DPM) is the most complex of diesel emissions. Diesel particulates, as defined by most emission standards, are sampled from diluted and cooled exhaust gases. This definition includes both solids, as well as liquid material which condenses during the dilution process. The basic fractions of DPM are elemental carbon, heavy HCs derived from the fuel and lubricating oil, and hydrated sulphuric acid derived from the fuel sulphur. DPM contains a large portion of the polynuclear aromatic hydrocarbons (PAH) found in diesel exhaust. Diesel particulates contains small nuclei with diameters below 0.04 μm, which agglomerate forming particles as large as 1 μm. The non-gaseous diesel emissions are grouped into three categories: soluble organic fraction (SOF), sulphate and soot [212].

Removal of the liquid fraction of PM is generally achieved by an oxidation catalyst. Oxidation catalysts have been fitted to US medium duty diesel vehicles since 1994 to reduce emissions of HC, the SOF content of DPM, and CO [212]. Typically, these catalysts are composed of $NM/CeO_2/Al_2O_3$ ($NM = Pt$) systems, where porosity of the catalysts often plays a key role since adsorption of the SOF at the support allows its conversion at catalytic sites and hence its removal before its desorption starts [212]. This is a critical aspect in the diesel exhaust removal due to the generally low temperatures (120–350 °C) of the diesel exhaust [213]. In fact, during the test cycle, the temperature of the catalyst may easily fall below the light-off temperature making necessary additions of an adsorbent, typically a zeolite. Oxidation catalysts promote the oxidation of HC and CO with oxygen in the exhaust to form CO_2 and H_2O. Fuel sulphur levels of maximum 500 ppm are required to avoid excessive production of sulphate based PM and to minimise catalyst deactivation by sulphur poisoning. Lower levels of sulphur (50 ppm) can increase the effectiveness of oxidation catalysts by up to 50% and contribute to greater durability. Oxidation catalysts have not generally been used in heavy vehicles with the exception of urban buses, and are not considered necessary to meet HC and CO requirements of future HD emission regulations.

Removal of soot may be achieved by means of filtration (Fig. 23) [214]. Even though different types of filters can be employed [215], the filtration efficiency is generally high. However, the continuous use under the driving conditions leads to filter plugging. Regeneration of the filter is therefore a crucial step of the soot removal systems. This can be achieved thermally, by burning the soot deposits on the filter, using, for example a dual filter systems such as depicted in Fig. 23. However, such systems may be adopted only in the trucks where space requirements are less stringent compared to passenger cars. In addition, there are problems arising from the high temperatures achieved during the regeneration step when the deposited soot is burned off. In fact, local overheating can easily occur leading to sintering with consequent permanent plugging of the filter. To overcome these problems, development of catalytic filters has attracted the interested of many researchers (for a recent review, see Ref. [214]).

A comprehensive discussion of the diesel particulate abatement systems is beyond the scope of this paper, however, it is important to quote some emerging technologies in this field, one of the most important being those of the CRT [216] and use of fuel additives that favour combustion of the soot deposited on the filter [217,218]. The concept of the so-called CRT has been pioneered by researchers from Johnson Matthey [216] and is based on the observation that NO_2 is a more powerful oxidising agent towards the soot compared to O_2. The concept of CRT is illustrated in Fig. 24: a Pt catalysts is employed in front of the filtering device in order to promote NO oxidation; in the second part of CRT, DPM reacts with NO_2 favouring a continuous regeneration of the trap. A major drawback of these systems is related to the capability of Pt catalysts to promote SO_2 oxidation as well. The sulphate thus formed is then deposited on the particulate filter interfering with its regeneration. Moreover, the NO_2 reacts with the soot to reform NO whilst reduction of NO_2 to N_2 would be the desirable process. Accordingly, it is expected that as the NO_x emission limits will be pushed down by the legislation, less NO will be available in the exhaust for soot removal, unless the engine is tuned for high NO_x emission that are used in the CRT and then an additional $DeNO_x$ trap is located after the CRT device.

Use of fuel additives, particularly those based on CeO_2, is another area of interest [219]. Rhodia has introduced these additives on the market which now

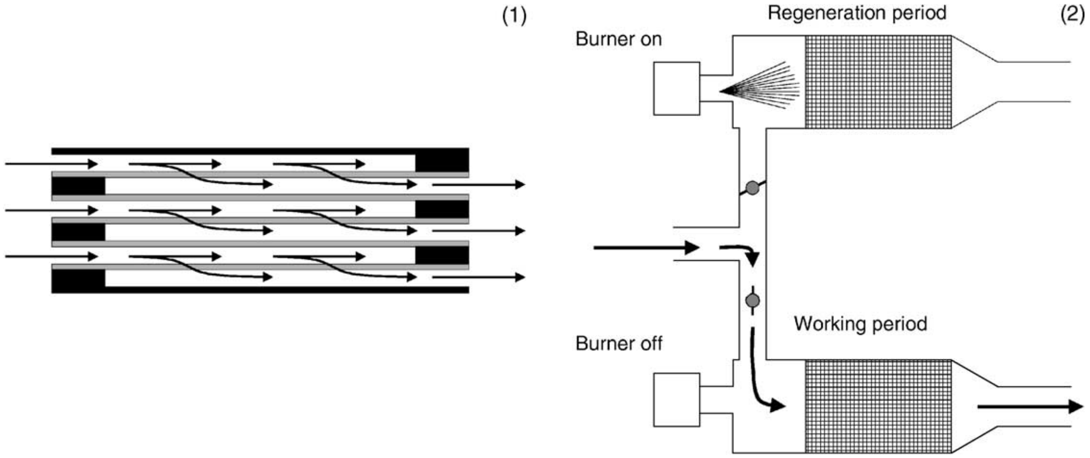

Fig. 23. Principle of filter operation (1) and filter re-generation (2) for a soot removal system, using fuel powered burners.

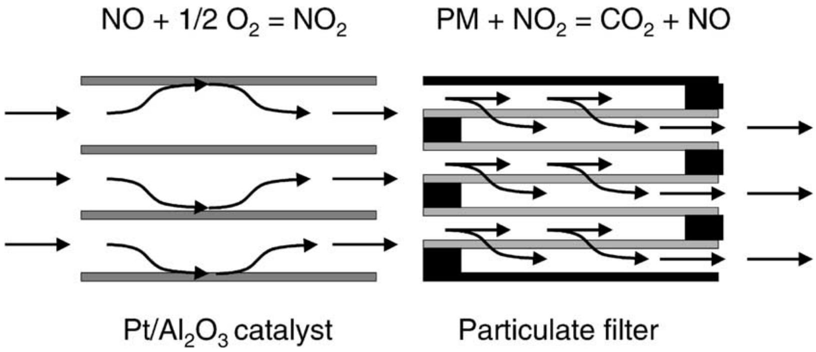

Fig. 24. The working principle of the continuously regenerating particulate trap.

have been applied in vehicles [217,218]. While there is a significant benefit in terms of promotion of the soot combustion from addition different additives even at very small concentrations [218], the environmental impact due the release of such additives into the atmosphere, following their widespread use, should be considered.

5. Conclusions

The development of automotive converters has proceeded by a continuous improvement of the catalytic performances and durability of the automotive catalysts over the past 25 years. Use of CeO_2–ZrO_2 technology represented a major improvement in terms of TWC durability in the last years, however, more and more demanding regulations are on the horizon. It is now clear that a TWC is a complex and integrated system that must be immediately effective and that its lifetime must be equivalent to that of the car. This demands new materials of extreme thermal stability, exceeding 1100 °C, which show extremely high conversions. The achievement of such targets require strong research efforts; a fundamental comprehension of the interactions between the NM and the other washcoat components and the deactivation phenomena is needed.

The requirements for more and more efficient engines highlights the problem of NO_x abatement under oxidising conditions. Even though huge efforts have been dedicated to development of lean-$DeNO_x$ catalysts, their durability and performances are still insufficient. Noticeably, of the different lean-$DeNO_x$ strategies for gasoline engines, the most effective and ready to use one is the so-called NSR concept which still uses a TWC to eliminate NO_x [112].

Technologies for control of particulate emissions from diesel engine will find increasing demand in the next years. In particular, catalytic filters will continue to be the subject of intense research.

Summarising, the end-of-pipe technologies for automotive pollution control, and in particular the TWC, have, and are, playing a key role in reducing air pollution. However, a new breakthrough point can be achieved only by adopting new strategies based more on prevention than on control. In this respect, it is important to highlight the great promise of hydrogen fuel cell technology [220]. The proton exchange membrane fuel cell—to make hydrogen from HCs—will be a major focus for research in electrocatalysis and catalytic fuel processing. It is worth noting that the targets obtained in the development of materials for TWCs constitutes an important scientific background for the design of new catalytic system for on-board hydrogen production. In fact, the on-board fuel reformer unit employs a number of catalytic steps involving reactions that routinely occur under the exhaust conditions and most of them appear to be promoted by the NM/CeO_2 interactions [13]. Consistently, M/CeO_2–ZrO_2 materials were reported to feature good activities for fuel reforming, WGS reaction and preferential CO oxidation [221–230]. However, further work is necessary to significantly enhance their performance, in order to obtain a miniaturisation of the system and therefore application in automobiles.

Acknowledgements

The authors gratefully thanks Dr. R. Di Monte, Prof. M. Graziani, University of Trieste, and Drs. P. Moles and C. Norman from MEL Chemicals for their valuable contribution to the development of the chemistry of CeO_2–ZrO_2 mixed oxides and helpful discussions. MEL Chemicals, University of Trieste, Fondo Trieste 1999, MURST-PRIN 2000 "Catalysis for the reduction of the environmental impact of mobile source emissions", CNR Agenzia 2000, INCA "Progetto Atmosfera Urbana" are gratefully acknowledged for financial support.

References

[1] J.C. Guibet, E. Faure-Birchem, Fuels and Engines: Technology, Energy, Environment, vol. 1, Editions Technip, Paris, 1999, pp. 1–385.
[2] R.J. Farrauto, R.M. Heck, Catal. Today 51 (1999) 351.
[3] M.L. Church, B.J. Cooper, P.J. Willson, SAE Paper 890815, 1989, p. 1.
[4] K.C. Taylor, Automobile catalytic converters, in: J.R. Anderson, M. Boudart (Eds.), Catalysis—Science and Technology, Springer, Berlin, 1984, Chapter 2, pp. 119–170.
[5] H. Bosch, Catal. Today 2 (1988) 369.
[6] K.C. Taylor, Catal. Rev.-Sci. Eng. 35 (1993) 457.
[7] M. Shelef, G.W. Graham, Catal. Rev.-Sci. Eng. 36 (1994) 433.
[8] M. Shelef, R.W. McCabe, Catal. Today 62 (2000) 35.
[9] P. Degobert, Automobiles and Pollution, Society of Automotive Engineers, Inc., Warrendale, PA, 1995.
[10] R.M. Heck, R.J. Farrauto, Catalytic Air Pollution Control: Commercial Technology, Van Nostrand Reinhold, New York, 1995, 1 pp.
[11] R.M. Heck, R.J. Farrauto, CATTECH 2 (1997) 117.
[12] A. Trovarelli, Catal. Rev.-Sci. Eng. 38 (1996) 439.
[13] J. Kaspar, M. Graziani, P. Fornasiero, Ceria-containing three way catalysts, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths: The Role of Rare Earths in Catalysis, Elsevier, Amsterdam, 2000, Chapter 184, pp. 159–267.
[14] M. Nuti, Emissions from Two-stroke Engines, Society of Automotive Engineers, Inc., Warrendale, PA, 1998, pp. 1–283.
[15] A. Walker, G. Chandler, J. Warren, C. Cooper, J. Harris, J. Thoss, A. Uusimeki, SAE Paper 01-0188, 2000.
[16] K.M. Adams, J.V. Cavataio, R.H. Hammerle, Appl. Catal. B 10 (1996) 157.
[17] M. Nonnenmann, SAE Paper 850131, 1985.
[18] S.T. Gulati, SAE Paper 850130, 1985.
[19] H. Bode (Ed.), Materials Aspects in Automotive Catalytic Converters, Wiley/VCH, Weinheim, Germany, 2002, pp. 1–281.
[20] S.T. Gulati, New developments in catalytic converter durability, in: A. Crucg (Ed.), Catalysis and Automotive Pollution Control, vol. II, Elsevier, Amsterdam, 1991, pp. 481–507.
[21] S. Eto, S. Yamamoto, Japan Patent N. JP-2000/26603 A2 155 9/5/2000.
[22] E.S.J. Lox, B.H. Engler, Environmental catalysis—mobile sources, in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), Environmental Catalysis, Wiley/VCH, Weinheim, Germany, 1999, Chapter 1, pp. 1–117.
[23] J.R. Anderson, Structure of Metallic Catalysts, Academic Press, London, 1975.
[24] F. Oudet, P. Courtine, A. Vejun, J. Catal. 114 (1988) 112.
[25] T. Horiuchi, Y. Teshima, T. Osaki, T. Sugiyama, K. Suzuki, T. Mori, Catal. Lett. 62 (1999) 107.
[26] F. Mizukami, K. Maeda, M. Watanabe, K. Masuda, T. Sano, K. Kuno, Preparation of thermostable high-surface-area aluminas and properties of the alumina-supported Pt catalysts, in: A. Crucg (Ed.), Catalysis and Automotive Pollution Control, vol. II, Elsevier, Amsterdam, 1991, pp. 557–568.
[27] L.L. Murrell, S.J. Tauster, Sols as precursors to transitional aluminas and these aluminas as host supports for CeO_2 and ZrO_2 microdomains, in: A. Crucg (Ed.), Catalysis and Automotive Pollution Control, vol. II, Elsevier, Amsterdam, 1991, pp. 547–555.
[28] N.A. Koryabkina, R.A. Shkrabina, V.A. Ushakov, M. Lausberg, F. Keptein, Z.R. Ismagilov, Kinet. Catal. 38 (1997) 112.
[29] Z.R. Ismagilov, R.A. Shkrabina, N.A. Koryabkina, D.A. Arendarskii, N.V. Shikina, Preparation of thermally stable washcoat aluminas for automotive catalysts, in: N. Kruse, A. Frennet, J.M. Bastin (Eds.), Catalysis and Automotive Pollution Control, vol. IV, Elsevier, Amsterdam, 1998, pp. 507–511.
[30] R. Di Monte, P. Fornasiero, J. Kaspar, M. Graziani, J.M. Gatica, S. Bernal, A. Gomez Herrero, Chem. Commun. (2000) 2167.
[31] A. Piras, A. Trovarelli, G. Dolcetti, Appl. Catal. B 28 (2000) L77.
[32] N.A. Koryabkina, R.A. Shkrabina, V.A. Ushakov, E.M. Moroz, M.F. Lansberg, Z.R. Ismagilov, Kinet. Catal. Engl. Transl. 37 (1996) 117.
[33] C. Morterra, G. Magnacca, V. Bolis, G. Cerrato, M. Barricco, A. Giachello, M. Fucale, Structural, morphological and surface chemical features of Al_2O_3 catalyst supports stabilized with CeO_2, in: A. Frennet, J.M. Bastin (Eds.), Catalysis and Automotive Pollution Control, vol. III, Elsevier, Amsterdam, 1995, pp. 361–373.
[34] C. Morterra, V. Bolis, G. Magnacca, J. Chem. Soc., Faraday Trans. 92 (1996) 1991.
[35] J.Z. Shyu, K. Otto, W.L.H. Watkins, G.W. Graham, R.K. Belitz, H.S. Gandhi, J. Catal. 114 (1988) 23.
[36] J.Z. Shyu, W.H. Weber, H.S. Gandhi, J. Phys. Chem. 92 (1988) 4964.
[37] J.M. Dominguez, J.L. Hernandez, G. Sandoval, Appl. Catal. A 197 (2000) 119.

[38] H.S. Gandhi, A.G. Piken, M. Shelef, R.G. Delosh, SAE Paper 760201, 1976, p. 55.
[39] M. Sideris, Methods for Monitoring and Diagnosing the Efficiency of Catalytic Converters: A Patent Oriented Survey, vol. 115, Elsevier, Amsterdam, 1997.
[40] J. Kaspar, P. Fornasiero, M. Graziani, Catal. Today 50 (1999) 285.
[41] R.W. McCabe, H.W. Jen, W. Chun, G.W. Graham, L.P. Haack, A. Straccia, D. Benson, Appl. Catal. A 184 (1999) 265.
[42] J.P. Cuif, G. Blanchard, O. Touret, A. Seigneurin, M. Marczi, E. Quémeré, SAE Paper 970463, 1997.
[43] W.D. Kingery, H.K. Bowen, D.R. Uhlmann, Grain growth, sintering and vitrification, in: Introduction to Ceramics, vol. 2, Wiley, New York, 1976, Chapter 10, pp. 448–515.
[44] D. Terribile, A. Trovarelli, J. Llorca, C. de Leitenburg, G. Dolcetti, Catal. Today 43 (1998) 79.
[45] C.E. Hori, H. Permana, K.Y.S. Ng, A. Brenner, K. More, K.M. Rahmoeller, D.N. Belton, Appl. Catal. B 16 (1998) 105.
[46] G.W. Graham, C.L. Roe, L.P. Haack, A.M. Straccia, J. Vac. Sci. Technol. A 18 (2000) 1093.
[47] P. Duwez, F. Odell, J. Am. Ceram. Soc. 33 (1950) 274.
[48] A.I. Leonov, E.K. Keler, A.B. Andreeva, Ogneupory 3 (1966) 42.
[49] A.I. Leonov, A.B. Andreeva, E.K. Keler, Izv. Akad. Nauk SSSR Neorg. Mater. 2 (1966) 137.
[50] E. Tani, M. Yoshimura, S. Somiya, J. Am. Ceram. Soc. 66 (1983) 506.
[51] G. Colon, M. Pijolat, F. Valdivieso, H. Vidal, J. Kaspar, E. Finocchio, M. Daturi, C. Binet, J.C. Lavalley, R.T. Baker, S. Bernal, J. Chem. Soc., Faraday Trans. 94 (1998) 3717.
[52] G. Colon, F. Valdivieso, M. Pijolat, R.T. Baker, J.J. Calvino, S. Bernal, Catal. Today 50 (1999) 271.
[53] T. Settu, R. Gobinathan, J. Eur. Ceram. Soc. 16 (1996) 1309.
[54] P. Vidmar, P. Fornasiero, J. Kaspar, G. Gubitosa, M. Graziani, J. Catal. 171 (1997) 160.
[55] G.L. Markaryan, L.N. Ikryannikova, G.P. Muravieva, A.O. Turakulova, B.G. Kostyuk, E.V. Lunina, V.V. Lunin, E. Zhilinskaya, A. Aboukais, Colloid Surf. A 151 (1999) 435.
[56] C.K. Narula, L.P. Haack, W. Chun, H.W. Jen, G.W. Graham, J. Phys. Chem. B 103 (1999) 3634.
[57] D. Terribile, A. Trovarelli, C. de Leitenburg, A. Primavera, G. Dolcetti, Catal. Today 47 (1999) 133.
[58] L.N. Ikryannikova, A.A. Aksenov, G.L. Markaryan, G.P. Muraveva, B.G. Kostyuk, A.N. Kharlanov, E.V. Lunina, Appl. Catal. A 210 (2001) 225.
[59] V. Perrichon, A. Laachir, S. Abouarnadasse, O. Touret, G. Blanchard, Appl. Catal. A 129 (1995) 69.
[60] G. Ranga Rao, J. Kaspar, R. Di Monte, S. Meriani, M. Graziani, Catal. Lett. 24 (1994) 107.
[61] P. Fornasiero, R. Di Monte, G. Ranga Rao, J. Kaspar, S. Meriani, A. Trovarelli, M. Graziani, J. Catal. 151 (1995) 168.
[62] G. Vlaic, P. Fornasiero, S. Geremia, J. Kaspar, M. Graziani, J. Catal. 168 (1997) 386.
[63] G. Balducci, J. Kaspar, P. Fornasiero, M. Graziani, M.S. Islam, J. Phys. Chem. B 102 (1998) 557.
[64] G. Balducci, M.S. Islam, J. Kaspar, P. Fornasiero, M. Graziani, Chem. Mater. 12 (2000) 677.
[65] G. Balducci, P. Fornasiero, R. Di Monte, J. Kaspar, S. Meriani, M. Graziani, Catal. Lett. 33 (1995) 193.
[66] N. Izu, T. Omata, S. Otsuka-Yao-Matsuo, J. Alloys Comp. 270 (1998) 107.
[67] R.T. Baker, S. Bernal, G. Blanco, A.M. Cordon, J.M. Pintado, J.M. Rodriguez-Izquierdo, F. Fally, V. Perrichon, Chem. Commun. (1999) 149.
[68] P. Fornasiero, J. Kaspar, M. Graziani, Appl. Catal. B 22 (1999) L11.
[69] M. Boaro, C. de Leitenburg, G. Dolcetti, A. Trovarelli, J. Catal. 193 (2000) 338.
[70] M. Yashima, H. Arashi, M. Kakihana, M. Yoshimura, J. Am. Ceram. Soc. 77 (1994) 1067.
[71] H.C. Yao, Y.F. Yu Yao, J. Catal. 86 (1984) 254.
[72] N. Hickey, P. Fornasiero, R. Di Monte, J. Kaspar, M. Graziani, G. Dolcetti, Catal. Lett. 72 (2001) 45.
[73] J. Kaspar, R. Di Monte, P. Fornasiero, M. Graziani, H. Bradshaw, C. Norman, Top. Catal. 16 (2001) 83.
[74] S.H. Oh, G.B. Fisher, J.E. Carpenter, D.W. Goodman, J. Catal. 100 (1986) 360.
[75] K.C. Taylor, J.C. Schlatter, J. Catal. 63 (1980) 53.
[76] B.K. Cho, J. Catal. 138 (1992) 255.
[77] B.K. Cho, J. Catal. 148 (1994) 697.
[78] R.W. McCabe, J.M. Kisenyi, Chem. Ind. London (1995) 605.
[79] J.C. Summers, W.B. Williamson, Palladium-only catalysts for closed-loop control, in: J.N. Armor (Ed.), Environmental Catalysis, American Chemical Society, Washington, DC, 1994, Chapter 9, pp. 95–113.
[80] D.D. Beck, J.W. Sommers, C.L. DiMaggio, Appl. Catal. B 11 (1997) 273.
[81] G.W. Graham, H.W. Jen, W. Chun, R.W. McCabe, J. Catal. 182 (1999) 228.
[82] M. Boaro, C. deLeitenburg, G. Dolcetti, A. Trovarelli, M. Graziani, Top. Catal. 16 (2001) 299.
[83] X.M. Song, A. Sayari, Catal. Rev.-Sci. Eng. 38 (1996) 329.
[84] A. Trovarelli, C. de Leitenburg, M. Boaro, G. Dolcetti, Catal. Today 50 (1999) 353.
[85] M. Waqif, P. Bazin, O. Saur, J.C. Lavalley, G. Blanchard, O. Touret, Appl. Catal. B 11 (1997) 193.
[86] S.H. Overbury, D.R. Mullins, D.R. Huntley, L. Kundakovic, J. Phys. Chem. B 103 (1999) 11308.
[87] A.E. Nelson, J. Yip, K.H. Schulz, Appl. Catal. B 30 (2001) 375.
[88] A.F. Diwell, R.R. Rajaram, H.A. Shaw, T.J. Truex, The role of ceria in three-way catalysts, in: A. Crucg (Ed.), Catalysis and Automotive Pollution Control, vol. II, Elsevier, Amsterdam, 1991, pp. 139–152.
[89] P. Bazin, O. Saur, J.C. Lavalley, G. Blanchard, V. Visciglio, O. Touret, Appl. Catal. B 13 (1997) 265.
[90] S. Hilaire, S. Sharma, R.J. Gorte, J.M. Vohs, H.W. Jen, Catal. Lett. 70 (2000) 131.
[91] T. Luo, J.M. Vohs, R.J. Gorte, J. Catal. 210 (2002) 397.
[92] R.M. Heck, R.J. Farrauto, Appl. Catal. A 221 (2001) 443.

[93] D.S. Lafyatis, G.P. Ansell, S.C. Bennett, J.C. Frost, P.J. Millington, R.R. Rajaram, A.P. Walker, T.H. Ballinger, Appl. Catal. B 18 (1998) 123.
[94] A.L. Boehman, S. Niksa, Appl. Catal. B 8 (1996) 41.
[95] J. Kaspar, P. Fornasiero, J. Solid State Chem. (2002), in press.
[96] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. 115 (1989) 301.
[97] M. Haruta, M. Date, Appl. Catal. A 222 (2001) 427.
[98] L.A. Petrov, Stud. Surf. Sci. Catal. C 130 (2000) 2345.
[99] J.R. Mellor, A. Palazov, B.S. Grigorova, J.F. Greyling, K. Reddy, M.P. Letsoalo, J.H. Marsh, Catal. Today 72 (2002) 145.
[100] S. Golunski, R. Rajaram, N. Hodge, G.J. Hutchings, C.J. Kiely, Catal. Today 72 (2002) 107.
[101] G.C. Bond, D.T. Thompson, Catal. Rev.-Sci. Eng. 41 (1999) 319.
[102] M. Iwamoto, H. Hamada, Catal. Today 10 (1991) 57.
[103] M. Shelef, Chem. Rev. 95 (1995) 209.
[104] K.A. Bethke, M.C. Kung, B. Yang, M. Shah, D. Alt, C. Li, H.H. Kung, Catal. Today 26 (1995) 169.
[105] J.N. Armor, Catal. Today 26 (1995) 147.
[106] Y. Traa, B. Burger, J. Weitkamp, Micropor. Mesopor. Mater. 30 (1999) 3.
[107] T.J. Truex, R.A. Searles, D.C. Sun, Plat. Met. Rev. 36 (1992) 2.
[108] J.N. Armor, Mobile engine emission control: an overview, in: J.N. Armor (Ed.), Environmental Catalysis, American Chemical Society, Washington, DC, 1994, Chapter 8, pp. 90–93.
[109] M.D. Amiridis, T.J. Zhang, R.J. Farrauto, Appl. Catal. B 10 (1996) 203.
[110] T. Kreuzer, E.S. Lox, D. Lindner, J. Leyrer, Catal. Today 29 (1996) 17.
[111] P. Zelenka, W. Cartellieri, P. Herzog, Appl. Catal. B 10 (1996) 3.
[112] A. Fritz, V. Pitchon, Appl. Catal. B 13 (1997) 1.
[113] P. Gilot, M. Guyon, B.R. Stanmore, Fuel 76 (1997) 507.
[114] H. Akama, K. Matsushita, Catal. Surv. Jpn. 3 (1999) 139.
[115] D.N. Belton, K.C. Taylor, Curr. Opin. Solid State Mater. Sci. 4 (1999) 97.
[116] M. Misono, T. Inui, Catal. Today 51 (1999) 369.
[117] The impact of sulfur in diesel fuel on catalyst emission control strategy, Report by Manufacturers of Emissions Controls Association, March 15, 1999, pp. 1–25.
[118] R. Burch, T.C. Watling, Catal. Lett. 37 (1996) 51.
[119] R. Burch, D. Ottery, Appl. Catal. B 9 (1996) L19.
[120] R. Burch, P.J. Millington, Catal. Today 29 (1996) 37.
[121] R. Burch, T.C. Watling, Catal. Lett. 43 (1997) 19.
[122] R. Burch, D. Ottery, Appl. Catal. B 13 (1997) 105.
[123] R. Burch, T.C. Watling, J. Catal. 169 (1997) 45.
[124] R. Burch, T.C. Watling, Appl. Catal. B 11 (1997) 207.
[125] R. Burch, J.A. Sullivan, T.C. Watling, Catal. Today 42 (1998) 13.
[126] R. Burch, P. Fornasiero, B.W.L. Southward, Chem. Commun. (1998) 625.
[127] R. Burch, P. Fornasiero, T.C. Watling, J. Catal. 176 (1998) 204.
[128] R. Burch, T.C. Watling, Appl. Catal. B 17 (1998) 131.
[129] R. Burch, E. Halpin, M. Hayes, K. Ruth, J.A. Sullivan, Appl. Catal. B 19 (1998) 199.
[130] R. Burch, P. Fornasiero, B.W.L. Southward, Chem. Commun. (1998) 739.
[131] R. Burch, P. Fornasiero, B.W.L. Southward, J. Catal. 182 (1999) 234.
[132] R. Burch, A.A. Shestov, J.A. Sullivan, J. Catal. 188 (1999) 69.
[133] R. Burch, J.A. Sullivan, J. Catal. 182 (1999) 489.
[134] R. Burch, A.A. Shestov, J.A. Sullivan, J. Catal. 186 (1999) 353.
[135] R. Burch, A.A. Shestov, J.A. Sullivan, J. Catal. 182 (1999) 497.
[136] A.A. Shestov, R. Burch, J.A. Sullivan, J. Catal. 186 (1999) 362.
[137] F.C. Meunier, J.P. Breen, V. Zuzaniuk, M. Olsson, J.R.H. Ross, J. Catal. 187 (1999) 493.
[138] B.K. Cho, J. Catal. 131 (1991) 74.
[139] J. Kaspar, C. de Leitenburg, P. Fornasiero, A. Trovarelli, M. Graziani, J. Catal. 146 (1994) 136.
[140] K.L. Roberts, M.D. Amiridis, Ind. Eng. Chem. Res. 36 (1997) 3528.
[141] A.A. Nikolopoulos, E.S. Stergioula, E.A. Efthimiadis, I.A. Vasalos, Catal. Today 54 (1999) 439.
[142] B.H. Engler, J. Leyrer, E.S. Lox, K. Ostgathe, Catalytic reduction of nitrogen oxides in diesel exhaust gas, in: A. Frennet, J.M. Bastin (Eds.), Catalysis and Automotive Pollution Control, vol. III, Elsevier, Amsterdam, 1995, pp. 529–547.
[143] V. Pitchon, A. Fritz, J. Catal. 186 (1999) 64.
[144] G.R. Bamwenda, A. Ogata, A. Obuchi, J. Oi, K. Mizuno, J. Skrzypek, Appl. Catal. B 6 (1995) 311.
[145] M. Inaba, Y. Kintaichi, H. Hamada, Catal. Lett. 36 (1996) 223.
[146] E. Guglielminotti, F. Boccuzzi, Appl. Catal. B 8 (1996) 375.
[147] J. Pasel, V. Speer, C. Albrecht, F. Richter, H. Papp, Appl. Catal. B 25 (2000) 105.
[148] G. Delahay, B. Coq, E. Ensuque, F. Figueras, Catal. Lett. 39 (1996) 105.
[149] Y. Liu, B. Zhong, S.Y. Peng, Q. Wang, T.D. Hu, Y.N. Xie, X. Ju, Catal. Today 30 (1996) 177.
[150] Y. Okamoto, H. Gotoh, H. Aritani, T. Tanaka, S. Yoshida, J. Chem. Soc., Faraday Trans. 93 (1997) 3879.
[151] Y. Okamoto, H. Gotoh, Catal. Today 36 (1997) 71.
[152] G. Delahay, E. Ensuque, B. Coq, F. Figueras, J. Catal. 175 (1998) 7.
[153] Y. Okamoto, T. Kubota, H. Gotoh, Y. Ohto, H. Aritani, T. Tanaka, S. Yoshida, J. Chem. Soc., Faraday Trans. 94 (1998) 3743.
[154] H. Aritani, S. Kawaguchi, T. Yamamoto, T. Tanaka, Y. Okamoto, S. Imamura, Chem. Lett. (2000) 532.
[155] A. Obuchi, I. Kaneko, J. Oi, A. Ohi, A. Ogata, G.R. Bamwenda, S. Kushiyama, Appl. Catal. B 15 (1998) 37.
[156] A. Abe, N. Aoyama, S. Sumiya, N. Kakuta, K. Yoshida, Catal. Lett. 51 (1998) 5.
[157] S. Kameoka, T. Chafik, Y. Ukisu, T. Miyadera, Catal. Lett. 51 (1998) 11.

[158] S. Kameoka, Y. Ukisu, T. Miyadera, Phys. Chem. Chem. Phys. 2 (2000) 367.

[159] M.F. Luo, X.X. Yuan, X.M. Zheng, Appl. Catal. A 175 (1998) 121.

[160] Y. Murata, S. Satokawa, K.I. Yamaseki, H. Yamamoto, H. Uchida, M. Yahagi, H. Yokota, AES 39 (1999) 447.

[161] S. Satokawa, Chem. Lett. (2000) 294.

[162] F.C. Meunier, J.P. Breen, J.R.H. Ross, Chem. Commun. (1999) 259.

[163] F.C. Meunier, V. Zuzaniuk, J.P. Breen, M. Olsson, J.R.H. Ross, Catal. Today 59 (2000) 287.

[164] F.C. Meunier, J.R.H. Ross, Appl. Catal. B 24 (2000) 23.

[165] V. Zuzaniuk, F.C. Meunier, J.R.H. Ross, Chem. Commun. (1999) 815.

[166] K.A. Bethke, H.H. Kung, J. Catal. 172 (1997) 93.

[167] T. Nakatsuji, T. Yasukawa, K. Tabata, K. Ueda, Assignee: JP 10244155 A2 (Issued: September 14, 1998); Priority: JP 97 47993 (Appl. Date: March 3, 1997), Sakai Chemical Industry Co. Ltd.

[168] E. Seker, J. Cavataio, E. Gulari, P. Lorpongpaiboon, S. Osuwan, Appl. Catal. A 183 (1999) 121.

[169] R.J. Farrauto, R.M. Heck, Catal. Today 55 (2000) 179.

[170] S. Naito, Y. Tanaka, Stud. Surf. Sci. Catal. 101 (1998) 1115.

[171] Q.W. Zhang, J. Li, X.X. Liu, Q.M. Zhu, Appl. Catal. A 197 (2000) 221.

[172] J.N. Hickey, P. Fornasiero, J. Kaspar, M. Graziani, G. Martra, S. Coluccia, S. Biella, L. Prati, M. Rossi, J. Catal. 209 (2002) 271.

[173] M. Misono, CATTECH 2 (1998) 53.

[174] T. Inui, S. Iwamoto, K. Matsuba, Y. Tanaka, Y. Yoshida, Catal. Today 26 (1995) 23.

[175] C. Rottlander, R. Andorf, C. Plog, B. Krutzsch, M. Baerns, Appl. Catal. B 11 (1996) 49.

[176] M. Iwamoto, H. Yahiro, H.K. Shin, M. Watanabe, J. Guo, M. Konno, T. Chikahisa, T. Murayama, Appl. Catal. B 5 (1994) L1.

[177] B.J. Adelman, W.M.H. Sachtler, Appl. Catal. B 14 (1997) 1.

[178] A. Ali, W. Alvarez, C.J. Loughran, D.E. Resasco, Appl. Catal. B 14 (1997) 13.

[179] H. Ohtsuka, T. Tabata, Appl. Catal. B 21 (1999) 133.

[180] H. Ohtsuka, T. Tabata, Appl. Catal. B 26 (2000) 275.

[181] S. Matsumoto, H. Watanabe, T. Tanaka, A. Isogai, K. Kasahara, Nippon Kagaku Kaishi 12 (1996) 997.

[182] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, K. Kasahara, Catal. Today 27 (1996) 63.

[183] H. Shinjoh, N. Takahashi, K. Yokota, M. Sugiura, Appl. Catal. B 15 (1998) 189.

[184] S. Hodjati, P. Bernhardt, C. Petit, V. Pitchon, A. Kiennemann, Appl. Catal. B 19 (1998) 209.

[185] S. Hodjati, P. Bernhardt, C. Petit, V. Pitchon, A. Kiennemann, Appl. Catal. B 19 (1998) 221.

[186] S. Hodjati, C. Petit, V. Pitchon, A. Kiennemann, Appl. Catal. B 27 (2000) 117.

[187] H. Mahzoul, J.F. Brilhac, P. Gilot, Appl. Catal. B 20 (1999) 47.

[188] A. Amberntsson, H. Persson, P. Engstrom, B. Kasemo, Appl. Catal. B 31 (2001) 27.

[189] S. Balcon, C. Potvin, L. Salin, J.F. Tempere, G. Djega-Mariadassou, Catal. Lett. 60 (1999) 39.

[190] E. Fridell, M. Skoglundh, B. Westerberg, S. Johansson, G. Smedler, J. Catal. 183 (1999) 196.

[191] E. Fridell, H. Persson, B. Westerberg, L. Olsson, M. Skoglundh, Catal. Lett. 66 (2000) 71.

[192] E. Fridell, H. Persson, L. Olsson, B. Westerberg, A. Amberntsson, M. Skoglundh, Top. Catal. 16 (2001) 133.

[193] P.H. Han, Y.K. Lee, S.M. Han, H.K. Rhee, Top. Catal. 16 (2001) 165.

[194] L. Lietti, P. Forzatti, I. Nova, E. Tronconi, J. Catal. 204 (2001) 175.

[195] F. Prinetto, G. Ghiotti, I. Nova, L. Lietti, E. Tronconi, P. Forzatti, J. Phys. Chem. B 105 (2001) 12732.

[196] F. Rodrigues, L. Juste, C. Potvin, J.F. Tempere, G. Blanchard, G. Djega-Mariadassou, Catal. Lett. 72 (2001) 59.

[197] P.J. Schmitz, R.J. Baird, J. Phys. Chem. B 106 (2002) 4172.

[198] P. Engstrom, A. Amberntsson, M. Skoglundh, E. Fridell, G. Smedler, Appl. Catal. B 22 (1999) L241.

[199] U. Gobel, J. Hohne, E.S. Lox, W. Muller, A. Okumura, W. Strehlau, M. Hori, SAE Paper 99FL-103, 1999.

[200] H. Hirata, I. Hachisuka, Y. Ikeda, S. Tsuji, S. Matsumoto, Top. Catal. 16 (2001) 145.

[201] S. Matsumoto, Y. Ikeda, H. Suzuki, M. Ogai, N. Miyoshi, Appl. Catal. B 25 (2000) 115.

[202] J.R. Asik, D.A. Dobson, G.M. Meyer, Soc. Automot. Eng. SP-1573 (2001) 111.

[203] B.H. Jang, T.H. Yeon, H.S. Han, Y.K. Park, J.E. Yie, Catal. Lett. 77 (2001) 21.

[204] S. Hodjati, K. Vaezzadeh, C. Petit, V. Pitchon, A. Kiennemann, Appl. Catal. B 26 (2000) 5.

[205] K. Nakatani, S. Hirota, S. Takeshima, K. Itoh, K. Tanaka, K. Dohmae, Soc. Automot. Eng. SP-1674 (2002) 57.

[206] P. Forzatti, Appl. Catal. A 222 (2001) 221.

[207] B. Amon, G. Keefe, Soc. Automot. Eng. SP-1626 (2001) 1.

[208] B. Amon, S. Fischer, L. Hofmann, R. Zurbig, Top. Catal. 16 (2001) 187.

[209] R. van Helden, M. van Genderen, M. van Aken, R. Verbeek, J.A. Patchett, J. Kruithof, T. Straten, C. Gerentet de Saluneaux, Soc. Automot. Eng. SP-1674 (2002) 15.

[210] T.V. Johnson, Soc. Automot. Eng. SP-1581 (2001) 23.

[211] S.M. Choi, Y.K. Yoon, S.J. Kim, G.K. Yeo, H.S. Han, Soc. Automot. Eng. SP-1581 (2001) 171.

[212] R.J. Farrauto, K.E. Voss, Appl. Catal. B 10 (1996) 29.

[213] J.C. Clerc, Appl. Catal. B 10 (1996) 99.

[214] B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, Catal. Rev.-Sci. Eng. 43 (2001) 489.

[215] P. Ciambelli, P. Corbo, V. Palma, P. Russo, S. Vaccaro, B. Vaglieco, Top. Catal. 16 (2001) 279.

[216] R. Allansson, P.G. Blakeman, B.J. Cooper, H. Hess, P.J. Silcock, A.P. Walker, SAE Paper SP-1673, 2002, 2002-01-428.

[217] E. AbiAad, R. Cousin, C. Pruvost, D. Courcot, R. Noirot, C. Rigaudeau, A. Aboukais, Top. Catal. 16 (2001) 263.

[218] S.J. Jelles, M. Makkee, J.A. Moulijn, Top. Catal. 16 (2001) 269.

[219] J.C. Summers, S. VanHoutte, D. Psaras, Appl. Catal. B 10 (1996) 139.

[220] D.L. Trimm, Z.I. Onsan, Catal. Rev.-Sci. Eng. 43 (2001) 31.

[221] G. Avgouropoulos, T. Ioannides, H.K. Matralis, J. Batista, S. Hocevar, Catal. Lett. 73 (2001) 33.

[222] I.H. Son, A.M. Lane, Catal. Lett. 76 (2001) 151.

[223] L. Basini, A. Guarinoni, A. Aragno, J. Catal. 190 (2000) 284.

[224] W.S. Dong, K.W. Jun, H.S. Roh, Z.W. Liu, S.E. Park, Catal. Lett. 78 (2002) 215.

[225] P. Pantu, K. Kim, G.R. Gavalas, Appl. Catal. A 193 (2000) 203.

[226] T. Bunluesin, R.J. Gorte, G.W. Graham, Appl. Catal. B 15 (1998) 107.

[227] J.A. Montoya, E. RomeroPascual, C. Gimon, P. DelAngel, A. Monzon, Catal. Today 63 (2000) 71.

[228] Q. Fu, A. Weber, M. Flytzani-Stephanopoulos, Catal. Lett. 77 (2001) 87.

[229] K. Li, Q. Fu, M. Flytzani-Stephanopoulos, Appl. Catal. B 27 (2000) 179.

[230] T.L. Zhu, M. Flytzani-Stephanopoulos, Appl. Catal. A 208 (2001) 403.

[231] P. Ciambelli, P. Corbo, M. Gambino, G. Minelli, G. Moretti, P. Porta, Catal. Today 26 (1995) 33.