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GUILLÉN-HURTADO, N.; RICO-PÉREZ, V.; GARCÍA-GARCÍA, A.; LOZANO-CASTELLÓ, D.;
BUENO-LÓPEZ, A.

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THREE-WAY CATALYSTS: PAST, PRESENT AND FUTURE.

N. GUILLÉN-HURTADO

Department of Inorganic Chemistry. University of Alicante. (Spain)

V. RICO-PÉREZ

Department of Inorganic Chemistry. University of Alicante. (Spain)

A. GARCÍA-GARCÍA

Department of Inorganic Chemistry. University of Alicante. (Spain)

D. LOZANO-CASTELLÓ

Department of Inorganic Chemistry. University of Alicante. (Spain)

A. BUENO-LÓPEZ.

Department of Inorganic Chemistry. University of Alicante. Alicante (Spain). agus@ua.es

RESUMEN: En este artículo de revisión se discute el pasado, presente y futuro de los catalizadores de tres vías. Se presentan las principales reacciones químicas que tiene lugar en los motor de gasolina así como las reacciones que ocurren en los catalizadores de tres vías (CTV) colocados en el escape, concretamente la oxidación de monóxido de carbonos e hidrocarburos y la reducción de los óxidos de nitrógeno a nitrógeno molecular. También se describen los principales componentes de un CTV (sustratos, metals nobles y óxidos de cerio). Por último se discute el problema del control de las emisiones en motores diesel, analizando la tecnología disponible en la actualidad para estos vehículos.

PALABRAS CLAVE: CTV, NO_x, oxidación CO, metal noble, óxido de cerio.

ABSTRACT: In this article, the past and the state-of-the-art in Three-Way Catalyst (TWC) technology are reviewed. The main chemical reactions occurring in a gasoline engine are discussed and also the main reactions taking place in a TWC placed in the tailpipe, namely CO and hydrocarbons oxidation and nitrogen oxides reduction to molecular nitrogen. The main components of a TWC (substrates, noble metals and cerium oxides) and their role in the different chemical reactions occurring in a TWC are described. Finally, the problem of diesel vehicles gas aftertreatment is described, and the current state-of-the art in catalytic converters for these vehicles are commented.

KEYWORDS: TWC, NO_x, CO oxidation, noble metal, cerium oxide.

1. INTRODUCTION

Gas pollution control in vehicles is a topic of ongoing research, since vehicles are among the main responsables of atmospheric pollution. The technology for exhaust purification is different for gasoline and Diesel engines. Gasoline engines exhaust consist of N₂, O₂, CO₂ and H₂O as main components together with some other undesired byproducts in much lower concentration, mainly CO, unburned hydrocarbons (HC) and NO_x. Diesel engine exhausts also yield N₂, O₂, CO₂ and H₂O, but in this case main pollutants are soot particles and NO_x (and few CO and unburned hydrocarbons). Pollution removal in gasoline vehicles is successfully accomplished with a Three Way Catalyst (TWC) which catalyzes the reactions between oxidizing (O₂ and NO_x) and reducing (CO and HC) species in the exhaust. This can be done because the concentration of oxidizing and reducing species are near the stoichiometric ratio. On the contrary, Diesel engines emit oxygen rich-

exhausts, where CO and HC can be oxidized quite easily while NO_x can be hardly reduced to N₂. In addition soot is a solid pollutant that needs a particular removal strategy.

In this article, the past, state-of-the-art, and future perspectives in the development of catalytic converters for vehicles are reviewed. TWC used in gasoline vehicles are first presented and gas pollution control in Diesel vehicles is discussed afterwards.

2. CHEMICAL REACTIONS.

The three major primary pollutants in the exhaust gases from gasoline vehicles are NO_x, hydrocarbons (HC) and carbon monoxide. Oxidation of gasoline in the engine to CO₂ and H₂O (equation 1) is not completely efficient, and due to this, the exhaust gas contains significant amounts of unburned hydrocarbons and partially combusted products like aldehydes, ketones, and carboxylic acids,

which are referred to as HC, together with large amounts of carbon monoxide (equation 2) [1].

gasoline (hydrocarbons) + O₂ →



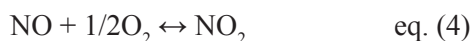
gasoline (hydrocarbons) + O₂ →



In addition, the high temperature reached in the cylinder during the combustion favors the reaction between the main components of air, N₂ and O₂, to yield NO (equation 3) [2].



NO is partially oxidized to NO₂ by O₂ in the tailpipe (equation 4), and due to this equilibrium, the mixture of NO + NO₂ is usually referred to as NOx.



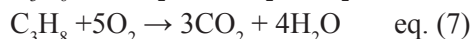
The NO-NO₂ equilibrium depends on temperature, partial pressures of the gases involved and contact time among them, and therefore changes along the tailpipe fluctuates depending on the running conditions.

Due to the aforementioned reactions, the main components of the exhaust gas of a gasoline vehicle are CO₂, H₂O, O₂, N₂, NOx, CO and HC, and among them, CO, HC and NOx must be removed because of their negative health and environmental impact. To accomplish this task, TWC are placed in the vehicle tailpipe to convert CO, HC and NOx into some other innocuous gas species. The main reactions taking place in a TWC are [1]:

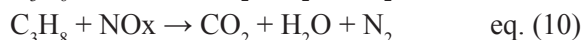
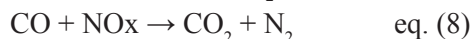
- Oxidation of carbon monoxide:



-Oxidation of hydrocarbons (C₃H₆ and C₃H₈ have been selected as examples):



- Reduction of NOx with CO and HC, which are oxidized (stoichiometric coefficients have not been included for NOx reactions because they depend on the particular NO/NO₂ ratio):



In addition to these reactions, it must be mentioned that H₂ is produced in a TWC by additional reactions, such as the so-called water gas shift reaction (WGS) between CO and

H₂O that yields CO and H₂ and by H₂O reaction with reduced ceria (see below). H₂ also contributes to NOx reduction, but the detailed analysis of these complex reaction pathways is beyond the scope of the current article.

3. THREE-WAY CATALYSTS (TWC).

The exhaust of a gasoline engine is a demanding environment that obligates TWC to operate at low temperature, withstand thermal peaks up to about 1000°C, tolerate the presence of poisons, especially sulfur species and lead (in the past), and not to be affected by gas flow pulsations and severe mechanical vibrations [1]. Catalytic systems were first introduced to control exhaust emissions in vehicles in the 1970s, and to fulfill all these requirements, the composition of TWC has been improved since early formulations.

As has been mentioned, the main reactions taking place in a TWC catalyst are the oxidation of carbon monoxide and hydrocarbons to carbon dioxide (and water) and the reduction of nitrogen oxides to molecular nitrogen. Current TWC are able to remove all these three pollutants simultaneously, and for this reason, they receive the name of Three-Way Catalysts. Application of TWC requires three elements [1]: (i) Electronic fuel injection (EFI) to provide a stoichiometric air/fuel mixture; (ii) an oxygen sensor in the exhaust and (iii) a microprocessor to control a feedback-loop using oxygen sensor signals to determine the amount of fuel to be injected under specific conditions to maintain the exhaust gas close to the stoichiometric point. By the early 1980s all of the elements necessary for the operation of TWCs were available.

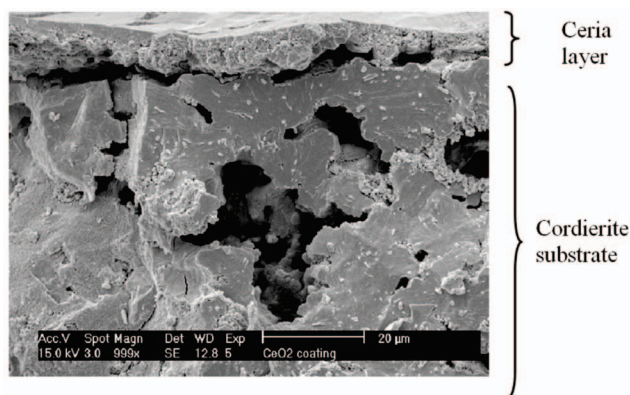


Figure 1. Microscopy picture of a cordierite substrate loaded with ceria (picture taken in a SEM microscope HITACHI S-3000N).

Most current TWC consist of a ceramic monolithic honeycomb where the different active phases are loaded. These active phases are mainly composed of noble metals, cerium-based oxides and alumina [1]. The active phases are loaded into the substrate as a thin layer (referred to as a washcoat), typically 10–150 μm thick. In the coming sections, the main components of such active phases and their role in the different chemical reactions occurring in a TWC are described.

As an example, Figure 1 shows a microscopy picture of a TWC prepared in our laboratory, where a detail of the cordierite substrate coated with a ceria layer is observed.

3.1 The substrates.

The main substrates used in TWC are ceramic monoliths.

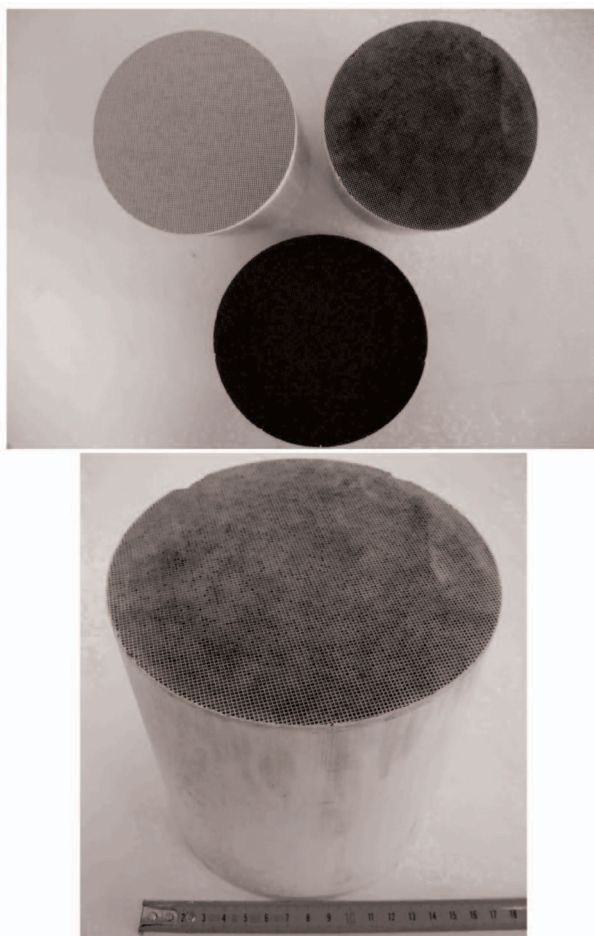


Figure 2. Bare and loaded cordierite honeycomb monoliths.

The monoliths are made from cordierite because this material has a very low thermal expansion coefficient, which is needed to prevent them from cracking when thermally stressed during use. Monoliths are manufactured by extruding a suitable mixture of clay, talc, alumina and water with various organic additives, which is dried and calcined at high temperature. During this process cordierite, $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, is formed [3].

Monolithic structures consist of blocks of small (0.5–4 mm) parallel channels. The very open structure of a monolith avoids fouling, as small particles easily travel through the channels, and the pressure drop produced in the gas stream is very low [4].

As example, Figure 2 shows pictures of different cordierite honeycomb monoliths. The white monolith (left; top) is a bare substrate and the remaining pieces have been loaded in our laboratory with different Pt and ceria containing active phases.

3.2. Noble metals: the main active components.

Early catalytic converters used in gasoline vehicles were designed to oxidize HC and CO, and transition metal catalysts like copper and nickel were tested. However, it was established that these metals were sensitive to poisoning by lead and halide from additives in the fuel, and also by sulfur dioxide derived from sulfur compounds originally present in the fuel and lubrication oils. Furthermore, they did not present good thermal resistance and durability [5].

Platinum group metal catalysts were found to be very active, but Ru, Ir, and Os all form volatile oxides and could not be used. Platinum, palladium and rhodium met the requirements of having the nobility to remain metallic under most operating conditions, and not yielding volatile oxides that led to metal loss, and these metals have been used in catalysts for vehicles since their introduction [5].

Frequently, two or more metals are used jointly and platinum/palladium was used in some of the early oxidation catalysts, as was platinum/rhodium that was also used under rich conditions for NO_x reduction. Today TWC most commonly contain palladium/rhodium although platinum/rhodium is still used in

some cars. Palladium and platinum are the active components for CO and HC oxidation and the main role of rhodium is in NOx reduction [5].

The first cars with oxidation catalysts injected air into the exhaust gas to provide oxygen for oxidation of HC and CO. These vehicles operated with excess fuel and therefore the exhaust gas was net reducing. These systems were not able to reduce NOx [1].

The first catalytic systems for converting HC, CO, and NOx employed a dual-bed converter in which NOx was reduced in the first bed and CO and HC were oxidized in the second bed, utilizing secondary air injected between beds. TWC for the simultaneous removal of CO, HC and NOx were commercialized by the middle 1980s [6]. TWC are still used today in gasoline vehicles, but with significant advances in three areas: catalyst technology, cold-start strategy, and air–fuel ratio control.

TWC available in the 1980s usually started working at around 200°C, and the catalyst required a period of 1–2 min to reach this temperature. During that time, up to 80% of hydrocarbons in a drive cycle are emitted [6]. In the 1990s zeolite based hydrocarbon trapping systems, electrically heated catalysts, and exhaust gas burner systems were investigated, but the preferred solutions were to develop extremely fast light-off catalysts, to modify the combustion strategy and to place the catalysts close to the engine exhaust manifold or downstream with insulated exhaust pipes to raise the gas temperature.

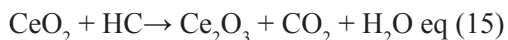
Most TWC formulations developed in the 1980s did not incorporate Pd because this metal is poisoned with lead and sulfur. This metal is less noble than Pt and thus more prone to interact with poison species. However, Pd is cheaper than Pt. The decreases in lead concentration in unleaded fuel throughout the 1980s allowed Pd utilization under three-way conditions, and in 1989 Pd/Rh catalysts were first commercialized, being still used today [5].

3.3. Cerium-based oxides: the oxygen storage components.

The air–fuel ratio control in gasoline vehicles is critical because TWC must operate at near stoichiometric concentration of reducing (HC + CO) and oxidizing (NOx + O₂) gas species in the exhaust. In order to adjust the

required air–fuel ratio an oxygen feedback control sensor was implemented, and also oxygen storage components were added to the catalyst to buffer the gas composition perturbations. The preferred oxygen storage component is ceria, and early TWC developed during the 1980s consisted of Pt and Rh dispersed on an alumina-coated cordierite monolith with ceria added for oxygen storage. The loading of ceria in these early TWC sometimes was up to 50% of the washcoat composition [1].

Ceria is able to store oxygen under oxidizing (equations 11, 12 and 13) conditions and involve the oxygen stored in the CO and HC oxidation reactions under reducing conditions (equations 14 and 15) due to the Ce⁴⁺/Ce³⁺ redox couple [7,8]. It is well established that lattice oxygen of ceria participates in these processes.



The actual importance of oxygen storage/release during dynamic operations is determined not only by the oxygen storage capacity of the cerium-based oxide but also by the rates of the cerium oxidation and reduction processes [7,8]. The oxidation process is faster than the reduction process, and consequently, the oxygen content of the catalyst will tend to remain high if the air–fuel ratio is cycled symmetrically about the stoichiometric point. In other words, the quasi-equilibrium oxidation state of Ce-containing catalysts under dynamic air–fuel ratio conditions is close to 4 [7].

In the early ceria-containing TWC was observed that thermal ageing lead to loss of noble metal–CeO₂ interactions, and simultaneously, a significant deactivation of the catalysts was observed. The deactivation was related to sintering of the noble metal particles leading to a loss of metal surface area and to the loss of CeO₂ surface area leading to a lower oxygen storage capacity (OSC). To overcome the problem of thermal deactivation, during the 1990s pure cerium oxide was replaced by CeO₂–ZrO₂ mixed oxides in TWC formulations. ZrO₂ improves the thermal stability and the oxygen storage capacity of CeO₂ [8]. In addition, the presence of ZrO₂ inhibits the undesirable interaction of CeO₂ with Al₂O₃, preventing the deactivation of the Ce⁴⁺/Ce³⁺ redox couple due to formation of CeAlO₃.

The high oxygen storage capacity of CeO_2 - ZrO_2 mixed oxides in comparison with pure ceria has been related to the high reducibility of Ce^{4+} in Zr-doped CeO_2 , which is a consequence of the high oxygen mobility inside the lattice. The reason for the increased mobility lies in the high defective structure and lattice strain, which is generated by introduction of the smaller isovalent Zr^{4+} cation into the CeO_2 lattice. Zr^{4+} has an ionic radius of 0.84 Å, smaller than 0.97 Å, found for Ce^{4+} in the same coordination environment [7].

In addition to the role as oxygen buffer, cerium-based oxides have also some other benefits in TWC performance, since they promote the noble metal dispersion, increase the thermal stability of the Al_2O_3 support by preventing the transformation of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$, promote the water gas shift and steam reforming reactions, favors catalytic activity at the interfacial metal-support sites, and promote CO removal through oxidation employing lattice oxygen [8].

The noble metal dispersion capacity of cerium oxides is observed in Figure 3, corresponding to a cordierite monolith loaded with a cerium oxide + Rh active phase in our laboratory. Figure 3a shows a SEM picture of the cordierite surface partially covered by active phase. The chemical mapping of this area evidences that dark areas are mainly cordierite, and high concentration of Si (element of cordierite) is found in these dark areas (Figure 3b). On the contrary, white areas are cerium oxide patches, which is evidenced in Figure 3c, and the similarity between Figure 3c (Ce) and Figure 3d (Rh) evidences that the noble is preferentially attached to cerium oxide rather than to cordierite. This preferential interaction of cerium oxides with noble metals promotes their dispersion, activity and stability.

4. FUTURE REQUIREMENTS: THE PROBLEM OF DIESEL VEHICLES.

Diesel engines are reliable, fuel efficient, durable, easy to repair, and inexpensive to operate. As a consequence of these advantages, diesel sales are growing, especially in Europe. However, emissions from diesel engines, mainly nitrogen oxides (NO_x) and particulate matter (soot) emissions, contribute to serious public health problems. CO and unburned hydrocarbons are also emitted by diesel engines, but in a significantly lower amount than those emitted by gasoline fuelled engines.

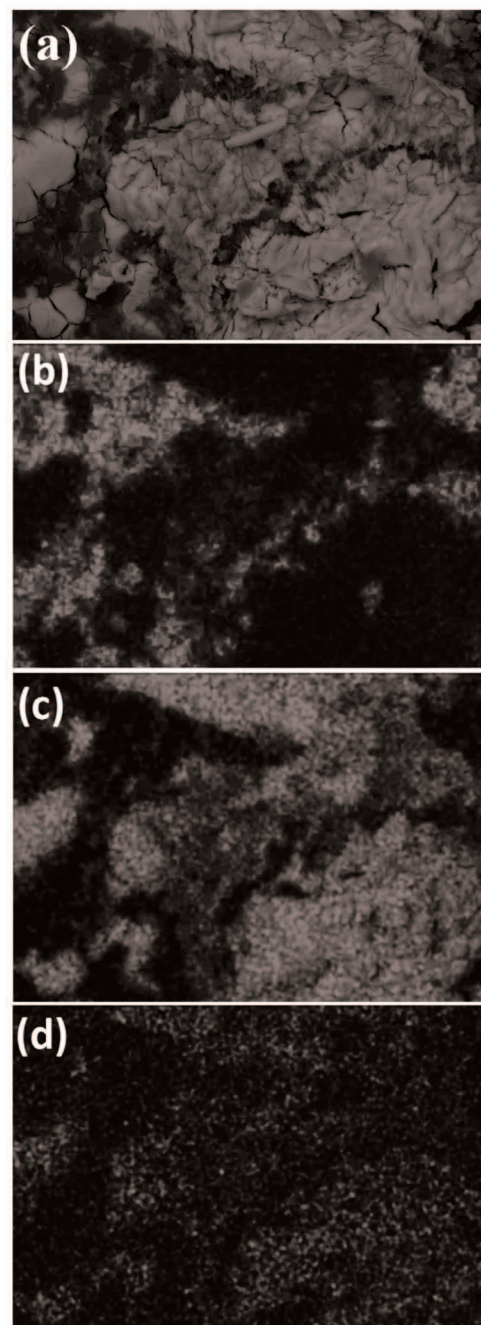


Figure 3. (a) Microscopy picture of a cordierite substrate loaded with ceria and Rh, and details of the chemical mapping of this area corresponding to Si (b), Ce (c) and Rh (d). (Images taken in a SEM microscope HITACHI S-3000N with an EDS analyser XFlash 3001 by Bruker for microanalysis and chemical mapping; The intensity of colours in Figures b, c and d is proportional to the concentration of each element).

Diesel vehicles had traditionally been considered clean in comparison with the gasoline vehicles [9], but the successful introduction of TWC for use in gasoline-

powered vehicles and the development of modern engines have changed this benefit of diesel engines. To search for removal techniques for diesel vehicles is an issue of current scientific and technological research.

4.1. Soot removal.

Soot is a solid pollutant that requires a particular removal strategy. Soot can be removed from the gas stream with the so-called diesel particulate filters (DPF), and as an example, Figure 4 shows a SiC DPF filter. This type of substrate consists of a honeycomb-like structure where 50% of the channels are plugged at the gas entrance side and remaining 50% are plugged at the opposite side. This obligates the exhaust gas to pass throughout the porous walls of the monolith, where the soot particles are filtered.

Once collected, soot must be combusted to avoid pressure drop in the exhaust [9,10]. The main problem is that the onset temperature for soot combustion ($> 500^{\circ}\text{C}$) is too high for spontaneous regeneration of the filters. DPF can be regenerated by post injection of fuel to raise the DPF inlet gas temperature [11], and this technology is commercially available. It has been extensively studied the regeneration of different filters made of highly stable materials, such as cordierite or SiC among other substrates, and has been observed [12] that the temperature inside the DPF can increase up to $1000\text{--}1100^{\circ}\text{C}$ as a consequence of the highly exothermal soot combustion process. Some authors suggest temperature gradients of $100^{\circ}\text{C}/\text{cm}$ along both radial and longitudinal directions of the DPF [13].

The catalytic combustion of soot has been also proposed for the regeneration of DPFs, and one of the challenges arising for the proper catalytic combustion of soot is the poor solid–solid contact between catalyst and soot in the DPF filters [13]. Several approaches have been proposed to overcome this problem. A precursor of the catalytically active component can be blended with fuel, and hence the catalyst is incorporated into the soot particle and ensures good contact. The most commonly used fuel additives are based on Ce, Pt, Cu, Fe, and Mn [10, 12–14]. Peugeot Citroën commercialized the fuel borne ceria catalyst and diesel particulate filter (DPF) to overcome the problem of poor contact [11].

It is also possible to improve the contact between soot and catalyst with a catalyst with low melting point or

high vapour pressure. This type of catalysts can be metal oxides with low melting temperatures, such as Sb_2O_3 , MoO_3 , V_2O_5 or PbO [15], alkali carbonates or hydroxides that form active and mobile alkali oxides or peroxides upon decomposition [13,16], chlorides of transition metals [17] and molten salts [18,19].

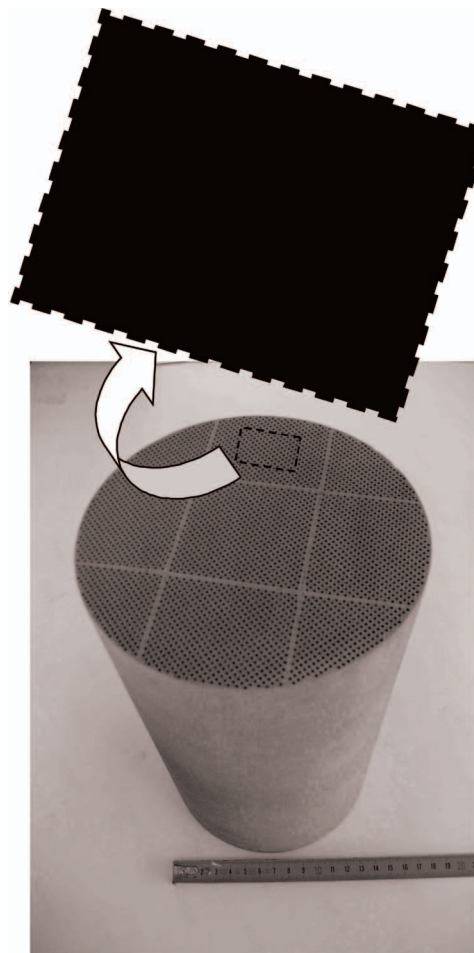


Figure 4. SiC Diesel Particulate Filter (DPF) and a detail of the top side of the filter, where open and plugged channels are distinguished.

Among the different catalytic after-treatment technologies proposed for soot removal in diesel exhausts, the so-called CRT (Continuously Regenerating Trap) seems to be the most satisfactory at this moment [1], especially for heavy-duty diesel applications. This system consists of a Pt catalyst for NO oxidation to NO_2 , which is more oxidizing than NO and O_2 [10,22,23]. The soot filter located downstream is continuously regenerated by soot oxidation to CO_2

using the previously produced NO_2 . However, the CRT system presents several drawbacks that need improvements, motivating fundamental and applied research work. NO_x removal over a CRT catalyst is somewhat less than 10% [1], and an additional system for NO_x removal is required. It is also reported that soot oxidation is strongly inhibited by the presence of SO_2 , so the CRT technology could not be commercialized until low sulfur diesel fuel became available [1]. In addition, because of the high price of noble metals new active components based on non-noble metals are desired, and other catalysts such as CeO_2 or Ce–Zr mixed oxides [22] have been also proposed.

4.2. NO_x removal.

The great difficulty of NO_x removal in diesel exhausts is that these gases, typically with a concentration of 0.01–0.1%, must be reduced to N_2 in a highly oxidizing atmosphere, with high O_2 concentrations (typically 5–20%).

NO_x can be converted into innocuous gases mainly by three ways [23]: (i) direct decomposition, (ii) selective catalytic reduction (SCR), or (iii) NO_x storage and reduction (NSR).

Although direct decomposition of NO is thermodynamically favorable and occurs without any reductant, the reaction possesses relatively high activation energy and this limits the practical use of this approach.

The SCR technology can be used to convert NO_x to N_2 in an O_2 -rich environment. SCR consist of selectively reducing NO_x with a reductant added in the exhaust. The SCR technology for diesel vehicles sources is based on the well-established technology used in power plants, where NH_3 or urea is injected in the postcombustion stream for NO_x reduction to N_2 [24,25]. The mainly used reductant for mobile sources is urea [26], but CO , H_2 and hydrocarbons have been also proposed as potential alternatives [27–29]. SCR requires a selective catalyst to promote the NO_x -reductant reaction in the presence of excess oxygen, and research is being carried out to develop such catalysts [1,30,31]. Among the most studied catalysts are those containing Pt and Ag.

The NSR technology is also suitable to convert NO_x

into N_2 . The NSR systems work under cyclic conditions of fuel lean and fuel rich environments. Under normal diesel vehicle operation (lean conditions) oxygen is in excess and NO_x is adsorbed on the catalyst. Periodically, a reductant is added, and under these rich conditions NO_x reduction takes place. A typical NSR catalyst combines a NO_x adsorption material, like alkali or alkaline earth metal compounds, with noble metals, which catalyse the oxidation of NO under lean conditions and the reduction of the stored NO_x under rich conditions.

Recently, Toyota corp. has developed a diesel particulate- NO_x reduction (DPNR) system and proposed that NO_x storage reduction catalysts can decrease soot oxidation temperature considerably [32]. These catalysts utilize both stored NO_x and active oxygen in decreasing soot oxidation temperature. The NO_x storage reduction catalysts have an advantage over conventional catalysts as they can also reduce NO_x ($\text{NO} + \text{NO}_2$) to N_2 .

5. CONCLUSIONS.

The past and the state-of-the-art in TWC technology have been reviewed. The main chemical reactions occurring in a gasoline engine have been discussed and also the main reactions taking place in a TWC placed in the tailpipe, namely CO and hydrocarbons oxidation and nitrogen oxides reduction to molecular nitrogen. The main components of a TWC (substrates, noble metals and cerium oxides) and their role in the different chemical reactions occurring in a TWC have been described. Finally, the problem of diesel vehicles gas after treatment and the current state-of-the art in catalytic converters for these vehicles have been commented.

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