

Twenty-five years after introduction of automotive catalysts: what next?

M. Shelef*, R. W. McCabe

*Chemical and Physical Sciences Laboratory, Ford Research Laboratory,
Ford Motor Company, MD-3179, SRL, PO Box 2053, Dearborn, MI 48121, USA*

Abstract

The union of catalysts and the automobile has been one of the greatest successes of heterogeneous catalysis over the last 25 years. Here, the history of automotive catalysis is briefly reviewed, followed by an assessment of where automotive catalysis stands today and where it is headed in the future. A key distinction between past automotive catalysis experience and that projected for the future is an increased focus on catalysts in upstream of power plant applications, such as on-board fuel processing units for fuel cell vehicles. Driven by ever tighter regulations, there will be continued research and development activity focused also on downstream applications (i.e. exhaust emission aftertreatment), especially for fuel-efficient, lean-burn vehicles, both *diesel* and spark-ignited. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Automotive catalysts designed to detoxify the exhaust were implemented in production in US on vehicles of the model year 1975 and, as we are reaching a full quarter century of their use, there is ample information available to allow us to declare that these devices, which are the principal emission control tools, have proved to be an unqualified success. Following the positive experience in US, in short order Japan and thereafter Europe, in 1986, adopted the use of automotive catalysts. Less affluent developing societies have come to the realization that emission control in heavily populated areas is not a costly frill but a tangible benefit for the quality of life and the use of automotive catalysts is rapidly spreading around the globe. Even a subjective, casual visitor to urban

centers where these devices have not yet been widely implemented will quickly notice the difference in air quality. The ubiquity of automobiles, and by extension of catalysts, has made catalysts and their function much more familiar to the population at large.

This paper, touches briefly on the development this scientific/technological effort has traversed, where it stands now, and what can be discerned on the horizon. The field is driven by environmental issues whose aim is to mitigate the undesirable side effects of modern lifestyle. Personal mobility is considered an essential part of this lifestyle and has come to be viewed as almost an inalienable right. The national and international regulatory bodies serve diligently as “enforcers” by promulgating ever more stringent emission rules so that the field of automotive catalysis is perpetually at the very edge of technology.

In the past, vehicular emission abatement was concerned mainly with (1) the residual uncombusted hydrocarbons (HC), (2) the partial combustion product — carbon monoxide (CO), (3) nitrogen oxides (NO_x)

* Corresponding author. Tel.: +1-313-337-4041;
fax: +1-313-248-5627.
E-mail address: mshelef@ford.com (M. Shelef).

formed from atmospheric nitrogen during combustion, and (4) particulate matter (PM), especially carbonaceous particulate formed in diesel engines. Presently the overriding concern is shifting to the unavoidable product of energy generation from carbonaceous fossil fuels — carbon dioxide (CO₂), a molecule whose concentration in the atmosphere has continuously risen since the beginning of the fossil fuels era and which, allegedly, is implicated in the “global warming” trend. It so happens that every remedy proposed to mitigate the amount of CO₂ produced by automotive vehicles is associated with a catalytic process, either on-board or off-board the vehicle. Hence, when discussing the developments on the horizon, we include these under the overall umbrella of automotive catalysts.

2. Early developments

The reader is referred to a number of previous reviews that treat in more detail developments during the early stages of automotive exhaust catalysis [1–6]. Here we confine ourselves to a brief recap of major issues and developments that shaped the course of technological development. The decision to put catalysts on vehicles was preceded by a lengthy gestation period during which a series of hurdles had to be overcome and there were also a few false starts. It had long been recognized, given a hot enough exhaust stream and an excess of oxygen, that several materials, especially noble metals and even some base metal combinations, might be sufficiently active to afford the oxidation of the unburned HC and CO on a catalyst placed in the exhaust downstream of the engine. To begin with, all the parties on whose business the implementation of catalytic exhaust after treatment impinged were concerned with the economic consequences. The overall perception was that the consumer would be saddled with excessive costs for measures whose actual value was not altogether clear. This perception was equally shared by the automotive industry and by the fuel producers, both of whose businesses would be affected. The apprehensions were many, the most prominent among these being: (a) can a catalyst survive the harsh environment of the exhaust?; (b) if not, because of the poisoning by lead, could the use of antiknock lead compounds in gasoline be dispensed with? (note that in its time the introduction of lead antiknock com-

pounds was hailed as a tremendous step forward which *inter alia* allowed the allied air superiority in WWII); (c) if base metals were not up to the task, lacking sufficient activity or being deactivated by sulfur, would there be enough affordable noble metals available?

Faced with the passage of laws stipulating definite limits on exhaust pollution, research efforts were redoubled and solutions to these problems gradually emerged. Lead was virtually legislated out of automotive fuel, this being based on its incompatibility with catalytic converters (although one can surmise that it would have been, in time, removed because of its adverse health effects). The octane quality of automotive fuels did not deteriorate as improved refining methods were implemented to compensate for the removal of lead. The list of catalytic elements having sufficient activity was indeed narrowed down to the noble metals and new mining and metal refining facilities were contracted for at affordable costs. The worries about irretrievably squandering a unique natural resource were, to a large extent, mitigated by the prospect of recycling the metals from converters removed from cars consigned to scrap. Finally, the survivability of the catalysts in the field was ascertained by field tests, including a 450-car field trial carried out by Ford in California in 1974 [7]. As is the case with every new technology, the early years of use witnessed catalyst failures due to misfueling, upstream engine and system malfunctions, etc., which were corrected as the experience with catalyst use was accumulated. At present, the reliability of catalysts equals that of other automotive components. This is an important issue since governmental regulations require proper functionality of emission systems for 100 000 miles of use (120 000 miles for trucks).

The combined requirements of compactness, high volumetric flow rates and low back pressure led to the adoption of a monolithic embodiment for automotive catalysts, quite different from the packed-bed forms that prevailed in almost all industrial and petroleum catalysis. The monoliths were multi-channeled ceramic catalyst bodies (square, triangular or honeycomb channel configurations), with the exhaust gas flowing through the channels on whose walls there is a coated high surface area porous layer with finely dispersed noble metal catalytic particles. (At the dawn of the implementation period, some manufacturers stuck to the more familiar granular catalysts. In use, these

catalyst granules or beads suffered from attrition and ultimately were abandoned in favor of the monoliths because of this and also poorer warm-up characteristics.) Presently, monolithic catalysts (mostly ceramic but also metallic in some special instances) are universally used in automotive catalysis. Moreover, the “monolith” catalytic technology is migrating into the realm of industrial catalysis, most often in processes for treatment of industrial effluents.

3. Which precious metals?

The choice of precious metals (synonymous to noble metals or platinum group metals) as the active catalytic materials in automotive materials was the result of three factors: (a) only the precious metals had the required activity needed for the removal of the pollutants in the very short residence times dictated by the large volumetric flows of the exhaust in relation to the size of catalyst which could be accommodated in the available space; (b) the precious metals were the only catalytic materials with the requisite resistance to poisoning by residual amounts of sulfur oxides in the exhaust; (c) the precious metals were less prone (but not entirely immune) to deactivation by high-temperature interaction with the insulator oxides of Al, Ce, Zr, etc., which constitute the so-called high surface area “washcoat” on which the active catalytic components are dispersed. While initially Pt and Pd in various proportions were used as oxidation catalysts, Rh was introduced with the advent of the three-way catalysts, having considerably better activity than Pt or Pd for the catalytic reduction of the oxides of nitrogen [8–11].

In a short time span, the automotive use of Rh accounted for the bulk of its production in the world and, since it is produced along with Pt at a more or less constant ratio, market demand created sharp price spikes. Pd has historically traded at much lower prices than Pt and Rh owing to sources outside South Africa, such as Russia, Canada, and US. Efforts to substitute Pd for Pt and/or Rh on a large scale were thwarted, however, by technical limitations, namely increased sensitivity of Pd relative to Pt and Rh to poisoning by lead and sulfur. By the late 1980s, residual lead levels in US unleaded gasoline had dropped to levels at which Pd could be implemented as a substitute for Pt. Ford introduced Pd/Rh catalysts in some of its models

in California in 1989, replacing the long-standing use of Pt/Rh in three-way catalysis (TWC) formulations. The use of Pd/Rh catalyst technology quickly spread within US, spurred on by improvements in techniques for segregating Pd and Rh into separate washcoat layers, this being to prevent the deleterious formation of bimetallic Pd–Rh particles. Introduction of Pd/Rh catalysts in Europe and other markets has been much slower due to a much more gradual process of eliminating the sale of leaded fuels.

A resurgence in environmental awareness in the late 1980s led US to the Clean Air Act of 1990 and a corresponding enactment of stricter emission regulations in Europe. These initiatives, in turn, greatly increased the worldwide demand for noble metals. While increased use of Pd as a substitute for Pt took some of the pressure off of Pt, Rh was still in very great demand and its price became unstable, peaking at \$7000/troy-oz in July of 1992 (compared to historical levels of ca. \$1000–\$1500). While the high prices were only temporary and to a large extent speculative, there was growing concern over the ability of the automotive industry to sustain long-term use of Rh at levels higher than the mine ratio. Clearly, an alternative to Rh was needed.

The alternative to Rh came in the form of Pd but Pd deployed in ways different than before, using considerably higher loadings. At one point, *Allied Signal* researchers claimed equivalence between a Pd-only catalyst at 56.7 g/ft³ loading and a 5:1 Pt/Rh catalyst at 20 g/ft³ [12]. New ways of promoting Pd were also developed, mostly involving rare earth oxides such as lanthana and ceria [13–15]. To a large extent, the use of Pd has benefited from the significant advances made in “oxygen storage” materials during the 1990s, as discussed below. However, it should also be noted that, in contrast to Pt (and Rh at levels normally employed), Pd itself contributes to oxygen storage by its ability to undergo a redox cycle under exhaust conditions. Our own work [16] has shown that this source of oxygen storage persists even under severe aging conditions in which the oxygen storage due to rare earth oxides is largely lost. This is shown in Fig. 1, in which the solid curve represents oxygen storage on Pd catalysts which contain no other oxygen storage agents. After 120 h of dynamometer aging, the Pd catalysts which contain rare earth oxides show no more oxygen storage than their ceria-free counterparts. Finally,

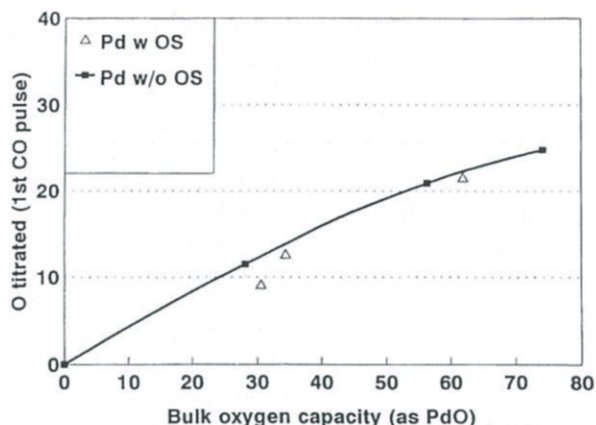


Fig. 1. O-atoms consumed (μmol O-atoms/g cat) in a pulse of CO flowed over a variety of TWCs containing different amounts of Pd. Filled squares: catalysts that contain no oxygen storage agents; triangles: dynamometer-aged catalyst containing oxygen storage agents (adapted from Ref. [16]).

given the high sensitivity of Pd to poisoning by sulfur [17–18], reduction of fuel sulfur to levels below 50 ppm in California reformulated fuels was another important factor in opening the door to widespread use of Pd-only catalysts.

Currently, TWC formulations containing Pt/Rh, Pt/Pd/Rh (trimetal), Pd-only, and Pd/Rh noble metal combinations are all in commercial use. It is not uncommon to find two formulations in use on the same vehicle (e.g. Pd-only as a light-off catalyst and Pd/Rh as downstream underbody catalyst). Issues of fuel quality (residual Pb levels, sulfur concentration) still play an important role in the choice of catalyst formulation for a particular market. As all of the formulations have improved over time, however, decisions regarding the choice of the noble metal and loading are becoming more and more based on cost factors. Indeed, with fluctuations in noble metal prices likely to persist into the future, one strategy for vehicle producers may be to have a number of available formulations “on the shelf” that can be deployed in response to changing market conditions.

4. Chemistry and electronics

That the catalyst performance is only as good as the “quality” of the exhaust gas mixture supplied to it is a truism of which all automotive catalyst researchers are

keenly aware. The earliest catalytic converters were designed solely for the oxidation of CO and HC and were generally used in conjunction with an air pump that ensured that, no matter how the engine was running, enough air was added to maintain excess oxygen required for efficient conversion. By the early 1980s, however, emission standards for NO_x in US had been tightened to the point where, for most vehicles, efforts to reduce NO_x emissions by lowering compression ratios or by exhaust gas recirculation were not sufficient and an NO_x catalyst was needed in addition for the CO and HC removal. Thus the era of TWC was ushered in. With TWC came a coupling of electronics and chemistry that, unlike many unions, has only strengthened with time.

As noted, CO and HC are converted under oxidizing conditions (i.e. with excess air) while NO_x is reduced to N_2 , requiring excess fuel. This is readily seen in a standard plot of conversion efficiency for the three species as a function of the mass air–fuel ratio (or alternatively, the λ value, which is the actual air–fuel ratio divided by the stoichiometric air–fuel ratio) as shown in Fig. 2a. Originally, these opposing conditions were met by dual-bed converters. Here the vehicle was operated to the rich side of the stoichiometric point and the front catalyst converted primarily NO. Air was then injected behind the front converter and the exhaust was led over a second catalyst to remove CO and HC. Dual-bed systems were far from

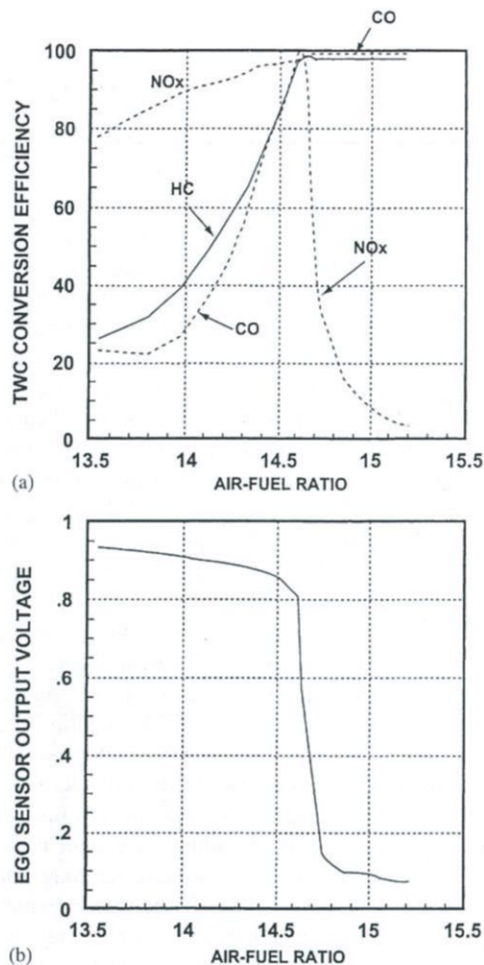


Fig. 2. (a) Typical TWC catalyst efficiency plot vs. air-fuel ratio. (b) The corresponding output voltage from the zirconia-based EGO sensor.

an optimal solution because a rich engine calibration adversely affected fuel economy and constrained the operating range of the engine. Moreover, under rich conditions, the reducing catalyst promoted significant conversion of NO_x to ammonia (NH₃) rather than the desired product, N₂. This in turn resulted in reconversion of ammonia to NO_x over the oxidizing catalyst limiting the effectiveness of the combined system [2].

It was recognized early that if the air-fuel ratio could be controlled sufficiently close to the stoichiometric value, all three pollutants could be converted (essentially equilibrated to CO₂, H₂O and N₂) with

high efficiency over a single catalyst [19]. Concurrent rapid developments in electronic processors and in gas sensors ushered in the era of closed-loop engine control. The basic scheme is to utilize an exhaust gas oxygen (EGO) sensor which senses at any given time whether the exhaust gas mixture is net-oxidizing (lean) or net-reducing (rich) and sends a signal back to the electronic engine control module. This module, in turn, signals the fuel injectors to increase or decrease the fueling rate as needed to drive the exhaust gas mixture back toward the stoichiometric point. Fig. 2b shows the typical switching characteristic of a zirconia-based exhaust gas sensor as a function of air-fuel ratio.

Throughout the 1980s and continuing today, huge advances have been made in emission control through the coupling of electronics and catalytic chemistry. Both hardware and software (i.e. calibration strategy) advances have narrowed the range of air-fuel ratio oscillations. At the same time, catalyst formulations have improved, through the addition of so-called "oxygen storage" components mentioned above, countervailing the residual excursions from the stoichiometric point. Fig. 3 shows typical air-fuel traces for a 1986 vehicle compared to a 1990 vehicle, with the typical range of air-fuel excursions in each case, mapped onto a plot of catalyst conversion efficiency vs. Air-fuel ratio. One notes the "tightening" of the air-fuel control which occurred over the four year period when carburetors and central fuel injector systems were replaced by multi-point fuel injectors, in some cases operated sequentially to coordinate fuel injection with the opening of cylinder intake valves. The aim is to supply just the right mix of air and fuel to each cylinder at just the right time to ensure stoichiometric combustion in each cylinder. These advances in fuel injection and air metering hardware have been matched by advances in control strategy, specifically improvements to the control algorithms introducing aspects of anticipatory control. By knowing the characteristic response times of fuel injectors and air flow rates, as induced for example by a sudden acceleration, it is now possible to compensate for these factors and maintain nearly stoichiometric exhaust gas mixtures even during highly transient driving modes.

Recent advances include control systems which add a second EGO sensor (or a heated EGO sensor)

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