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

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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)

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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 (CO_2), 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 CO_2 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 compounds 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,

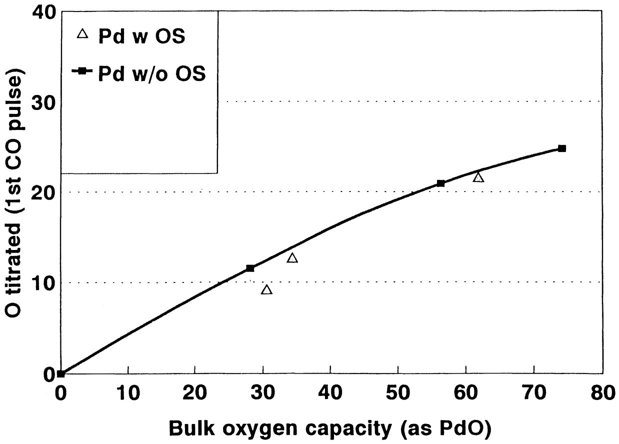

Fig. 1. O-atoms consumed (μmol O-atoms/g cat) in a pulse of CO flowed over a variety of TWCs containing different amounts of Pd. Filled squares: catalysts that contain no oxygen storage agents; triangles: dynamometer-aged catalyst containing oxygen storage agents (adapted from Ref. [16]).

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 vehicles 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

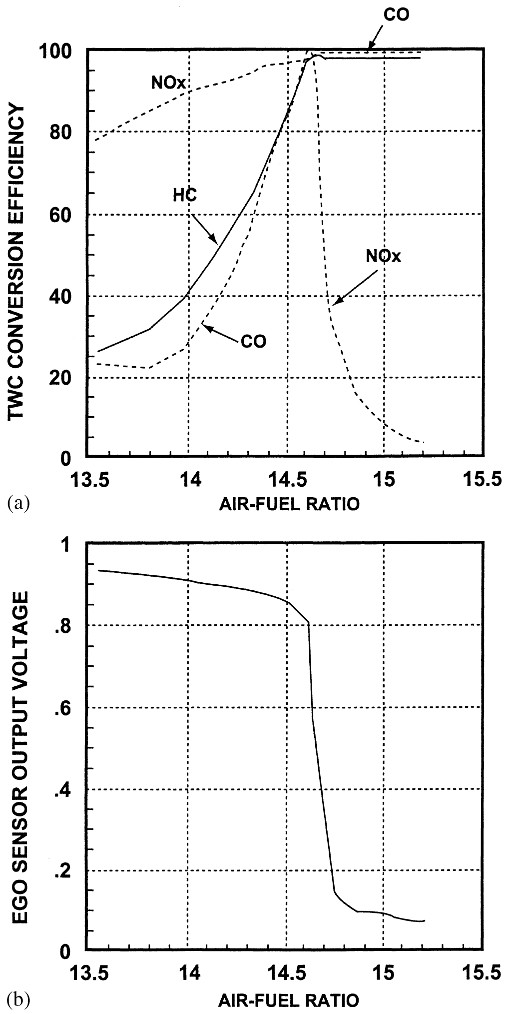

Fig. 2. (a) Typical TWC catalyst efficiency plot vs. air–fuel ratio. (b) The corresponding output voltage from the zirconia-based EGO sensor.

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 (NH_3) rather than the desired product, N_2. 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 CO_2, H_2O and N_2) 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)

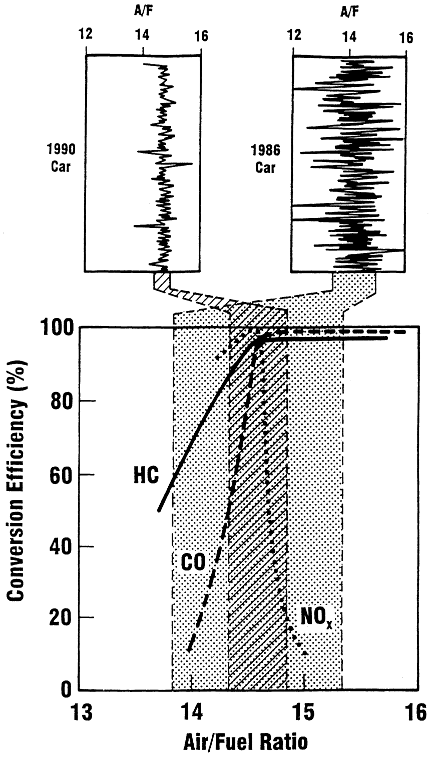

Fig. 3. Typical TWC conversion efficiency plot for HC, CO, and NO_x as a function of air–fuel ratio. Also shown are representative air–fuel ratio vs. time traces for 1986 and 1990 vehicles with the control bandwidth mapped onto the catalyst efficiency plot.

behind the catalyst in addition to the main controlling sensor upstream of the catalyst [20]. The downstream sensor is less prone to thermal aging or contamination, and also senses a more fully equilibrated exhaust gas mixture than the upstream sensor. Hence, it switches at a gas composition more representative of the true stoichiometric mixture and is used to correct the switch point of the main controlling sensor, particularly as that sensor ages. A rough block diagram for such a fore-aft oxygen sensor system is shown in Fig. 4.

A similar front and rear oxygen sensor configuration is also used to satisfy one of the on-board diagnostic requirements (OBD) specified by US EPA — that of catalyst efficiency monitoring. The strategy relies on the fact that a highly efficient catalyst has a large damping effect on the switching characteristics of a downstream sensor, whereas a deactivated catalyst causes relatively little damping. It is thus possible to compare the responses of upstream and downstream sensors and infer the activity of the catalyst. Such a system can be used to activate a dashboard light which notifies the driver of potential problems with the catalyst.

The coupling of electronics with chemistry for optimum emissions control is one research direction which will remain a fertile ground far into the future. As on-board computational capabilities continue to increase, more sophisticated control strategies will be implemented. As noted below, the cold-start period and periods of highly transient driving will be the focus of further work. In addition, greater capability will be developed to incorporate learning and self-diagnostic features into the control strategy which will allow the system to compensate for mileage induced changes in catalyst activity and in the sensor response characteristics.

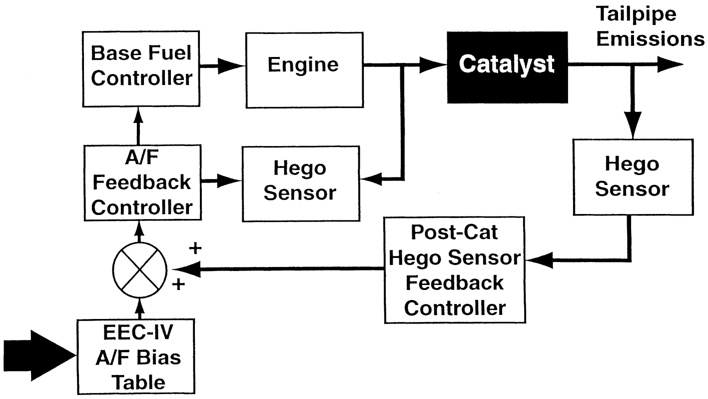

Fig. 4. Block diagram of a modern engine control system employing both pre- and post-catalyst heated EGO (HEGO) sensors.

5. Advances in "oxygen storage"

The concept of storing oxygen to buffer the lean-rich swings in exhaust gas composition during vehicle operation has been actively pursued since the earliest days of "three-way" automotive catalyst research, pre-dating the first commercial application of TWCs in the early 1980s [21,22]. Early on, ceria was recognized as a promising storage material because of its combination of facile redox cycling between the trivalent and tetravalent oxidation states of the Ce ions, good thermal stability, ease of impregnation onto alumina, and compatibility with noble metals. For many years, ceria has been the chief oxygen storage component for three-way catalysts and the mechanisms by which it works have been the subject of many studies and excellent review papers, including a recent detailed survey by Trovarelli [23]. Given the large body of information that exists, we confine our discussion to a brief summary of the most important commercial advances in oxygen storage technology over the years as reflected in three main eras, each associated with a distinct technological advance and a step-function improvement in TWC performance.

The first era of ceria-containing TWCs spanned roughly the years 1981–1985. At that time the TWC formulation was relatively simple. The catalysts contained noble metals impregnated onto either alumina pellets or an alumina washcoat on a monolithic substrate. Ceria was co-impregnated onto the alumina (at a few wt.%) along with the noble metals. Even this rudimentary addition of ceria dramatically improved TWC performance. Laboratory data of Kim [24], for example, comparing Pt–Pd–Rh/Al_2O_3 catalysts with and without 3 wt.% ceria after 24 h exposure to air at 932°C gave a 15–20% increase in the CO–NO *cross-over* efficiency with the addition of ceria. Kim's data also showed little benefit of ceria in promoting HC conversion, except under rich conditions in which steam reforming is promoted by the ceria.

The second period of ceria deployment was that of the so-called "high-tech" three-way catalysts, roughly between 1986 and 1992. Although "high-tech" was a designation that was inclusive of a number of advances in the TWC, the main one was the use of more ceria. The effectiveness of ceria as an oxygen storage component lies in its ability to store and supply oxygen to the noble metals on which the oxidation of CO proceeds. For pure ceria and ceria supported on alumina, this transfer is primarily via oxygen from the surface or near-surface region of the ceria. Thus, much of the emphasis in the design of the "high-tech" TWCs was on increasing the surface area of ceria in contact with the noble metals. Although surface impregnation onto alumina was still the main mode of deploying the ceria, loadings of ceria in some catalysts were increased to levels approaching 50% that of alumina by using physical mixtures of alumina and ceria particles. Again, the improvements in emission control were dramatic. Data of Williamson et al. [25], reproduced in Fig. 5, are representative of the levels of NO_x conversion that could be achieved by increasing the ceria content by a factor of 3 over base levels.

The success of the high-tech formulations could be weighed against an unintended consequence they produced for automobile manufacturers: the rotten egg odor associated with hydrogen sulfide (H_2S) formation. Here the problem was one of sulfate storage on ceria under lean operating conditions and subsequent reduction to H_2S under rich conditions. In US, the answer to the H_2S odor problem has been to incorporate nickel into the three-way catalyst formulation. The nickel acts as a scavenger for the sulfur (believed to be stored as NiS under rich conditions), and then releases it as SO_2 under lean conditions [26]. In Europe, concerns over the potential formation of poisonous nickel carbonyl, although never substantiated in practice, have led either to the use of other H_2S scavengers or to thermal pretreatment of the catalyst to reduce the ceria surface area.

The formation of H_2S was a problem of a "fresh" catalyst. The H_2S odor would go away with use as the ceria lost surface area through thermal sintering. The tendency toward thermal sintering, however, revealed a fundamental limitation of the "high-tech" catalyst formulations; they deactivated rapidly when exposed to exhaust gas temperatures in excess of about 800°C. The primary deactivation mechanism involved sintering of both the noble metals and the ceria, with concomitant loss of contact area between the two [27]. Fig. 6, for example, shows the growth of large ceria particles (as tracked by X-ray diffraction) for high-tech Pd/Rh and Pt/Rh catalyst formulations as a function of accumulated aging time in the lab (Fig. 6a) or on a vehicle (Fig. 6b). Transmission electron microscope characterization of noble metal particle sizes

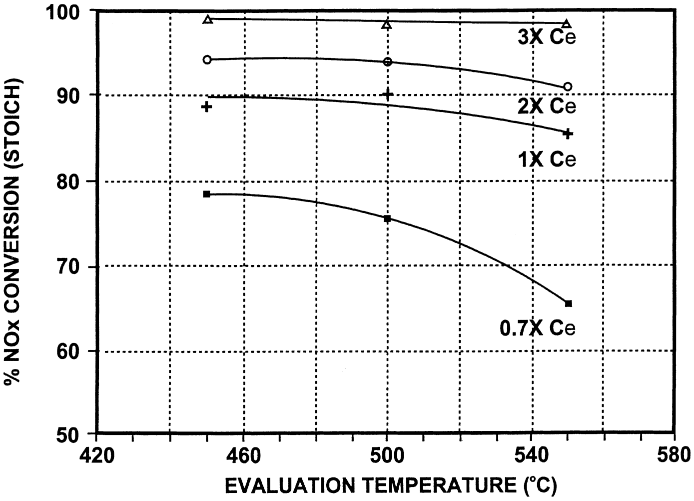

Fig. 5. NO_x conversion efficiency as a function of evaluation temperature for Pt/Rh TWCs differing in their amount of ceria relative to a base level (1X Ce) (adapted from Ref. [25]).

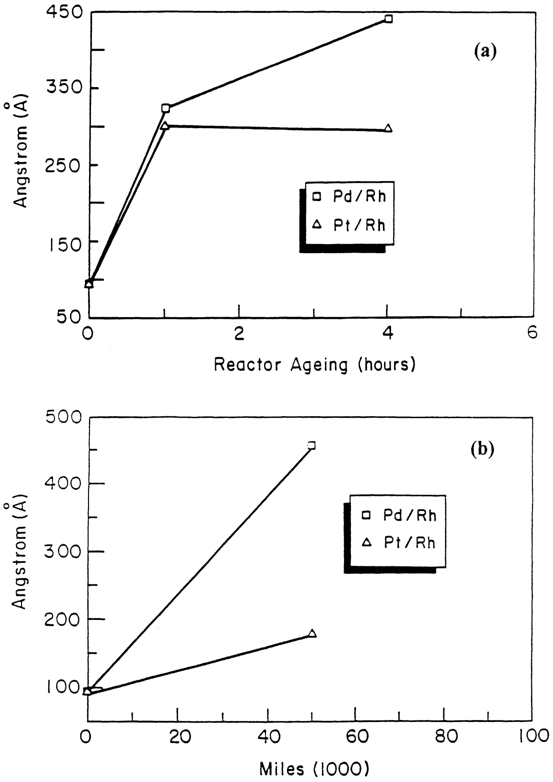

Fig. 6. CeO_2 particle size analysis (by X-ray diffraction) of (a) reactor aged and (b) vehicle aged high-tech Pd/Rh and Pt/Rh TWCs (adapted from Ref. [27]).

also revealed extensive sintering of the noble metal particles, and the temperature-programmed reduction (TPR) trace showed loss of features associated with "interactions" between the noble metal and ceria.

The thermal deactivation problems of the TWCs having high ceria loadings, together with a new push at the beginning of the 1990s for lower emissions, and an increase in US durability requirements from 50 000 to 100 000 miles, all called for new "oxygen storage" technology. The lower emissions standards brought about by new Federal, California, and European legislation in the early 1990s also amplified the importance of mounting the catalyst close to the engine to improve cold start emissions. This exacerbated the durability problems with the high ceria formulations as they were now required to operate in a hotter environment close to the exhaust manifold.

The solution to this problem was achieved by ceria stabilization. The ceria is stabilized by another metal oxide forming a solid solution with it. This is done through the use of pre-formed powders and, in some cases, by co-impregnation of the oxide precursors onto alumina. Like many advances in automotive catalysis, the exact source of this invention is difficult to identify. The first published paper showing improvements in engine dynamometer catalyst performance linked with direct evidence for improved oxygen adsorption characteristics and smaller CeO_2 crystallite sizes is probably that of Funabiki and Yamada [28]. The incorporation of stabilized cerias into automotive catalysts was a major advance in the ability of TWCs to perform at high efficiency even after severe thermal aging. Bartley et al. [29], for example, tested catalyst formulations containing stabilized ceria vs. a high standard ceria TWC after aging for 45 h at 1050°C. In federal test procedure (FTP) tests, catalysts containing stabilized ceria decreased the amount of unconverted NO_x to 15% of the engine-out level (compared to 22% of the engine-out level for the standard catalyst). The corresponding reductions for CO were 12 and 20%, respectively. Consistent with this, they also reported smaller ceria particle sizes in the case of the stabilized ceria (12.5 nm) compared to the standard catalyst (20 nm).

Although stabilization of ceria particle size (i.e. dispersion) by the addition of secondary oxides is important, it is not the only effect associated with the formation of solid-solution oxygen storage agents. Recent work in our laboratory, in collaboration with Rhodia, has shown that solid solutions of ceria and zirconia provide greatly enhanced participation by oxygen from the *bulk* of the ceria–zirconia particles compared to pure ceria [30,31]. For a model Pd catalyst supported on 70 wt.%-ceria–30 wt.%-zirconia, a TPR scan after 1050°C (and even 1150°C) aging (Fig. 7) shows the presence of a new peak between 100 and 200°C, not seen in the corresponding TPR of Pd on pure ceria. The new peak is due to oxygen supplied from the bulk of the ceria–zirconia particles. This relaxes the constraint of maintaining high surface area. Current research on further improving the thermal stability of “oxygen storage” components is directed at optimizing such factors as synthesis procedures, the composition of the mixed oxide materials and the role of additional surface and bulk promoters. Ultimately, the goal is to develop oxygen storage materials which are so stable that they can be used in any exhaust system location without deactivation over the life of the vehicle and without any need to “limit” exhaust temperatures [32]. Currently available pre-formed powders of stabilized ceria come close to meeting the desired performance and durability goals, certainly when tested with low-sulfur fuels.

6. Cold start

Another truism of automotive emissions catalysis is that the “game” of very low emissions is won or lost during the brief period (30 s or so) following cold

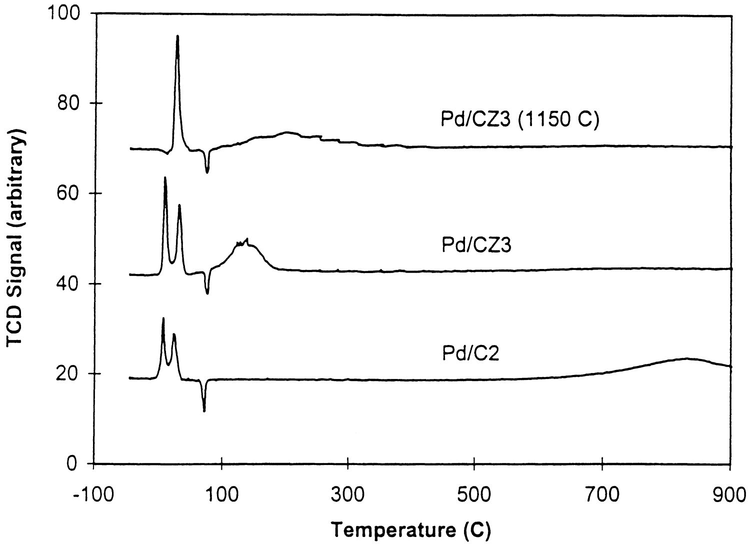

Fig. 7. Hydrogen-TPR traces of 1050°C redox-aged samples of 2% Pd on C2 (100% ceria) and CZ3 (70%-ceria–30%-zirconia) supports. Data also shown for the 2% Pd/CZ3 catalyst after 1150°C redox aging (from Ref. [31]).

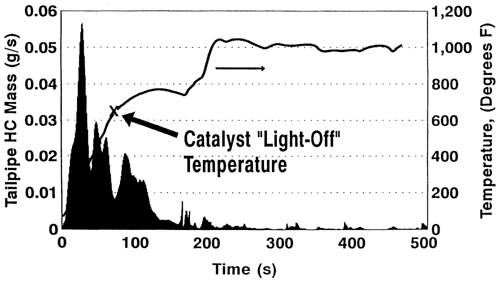

Fig. 8. Tailpipe HC emission rate (g/s) and catalyst temperature (°F) as a function of time following cold start in US FTP for a Ford 4.6L vehicle.

starting of the engine. Since the regulatory tests (e.g. US, European, and Japanese) register emissions from the instant of engine ignition, automotive catalytic converters, unlike industrial catalytic processes, do not have the luxury of being brought slowly on stream and lined out at steady-state operation. Thus, the challenge is to get the catalyst up to working temperatures (ca. 300°C) as quickly as possible. Fig. 8 shows cold-start emissions data for a Ford Crown Victoria vehicle tested on the US FTP cycle. The tailpipe HC emission rate is given as a function of time from the beginning of the test. Also shown is the catalyst temperature as a function of time. It can readily be seen that most of the HC emission over the full 505 s period occurs in the first 30–60 s as the catalyst is warming up to its operating temperature.

A number of approaches have been considered in recent years to improve emissions control, especially for HC, during the initial stages of the emission tests. Heat losses from the exhaust gas have been decreased by employing stainless steel exhaust manifolds rather than cast iron and a short double-wall air-gap exhaust pipe connecting to the exhaust manifold. Although the latter is extremely effective in improving the so-called “light-off” time of the catalyst system, such “close-coupling” also means that the catalyst must be able to withstand the extremely high temperatures that can sometimes occur near the manifold location. As noted above in the discussion of oxygen storage materials, this in turn has led to much effort to design catalysts that can withstand extreme exhaust gas temperatures up to about 1100°C. A second broad approach to decreasing cold-start emissions is to modify the operation of the engine during cold-start so as to dump more heat into the exhaust gas. This can be done, for example, by retarding the spark timing, thereby delaying combustion to later in the cycle and promoting carryover combustion in the exhaust ports. Also, catalyst light-off for HC and CO is favored by lean exhaust gas compositions and strategies are being developed that will allow the vehicle to be operated slightly lean of stoichiometric during cold-start while still affording good cold-start driveability.

In addition to engine and exhaust system modifications, the monolithic bodies of the catalysts have also undergone changes which improve their light-off performance. Much effort has been put into the design of thin-wall, high cell density substrates (both ceramic and metallic) that warm up faster and increase the surface area available for catalytic reactions. Likewise, catalyst formulations are being modified to improve their light-off characteristics, highly loaded Pd-only catalyst formulations representing one example of catalysts with improved light-off.

In the event that efforts to decrease heat losses, modify combustion and redesign catalysts to improve light-off initiation are not sufficient, additional devices such as electrically heated catalysts, hydrocarbon adsorbers and fuel-burning catalyst heaters offer additional possibilities for decreasing cold-start emissions. Thus far, there has been little need to employ these add-on devices as improvements resulting from the more conventional (and passive) approaches have been sufficient to maintain pace with ever stricter standards. However, in the limit of *zero* emissions, these additional devices will be needed.

7. Automotive catalysis under lean conditions

The operating conditions of the TWC at stoichiometry are very narrowly defined. This precludes taking advantage of operating the vehicle under lean conditions, i.e. using a large excess of air, where there is an opportunity to improve the fuel economy because of: (1) lower pumping losses; (2) a higher ratio of the constant-pressure to constant-volume specific heats of the burnt gas; (3) reduced heat loss to the walls of the combustion chamber. The diesel cycle uses a large excess of air and is more efficient than the Otto cycle of the gasoline-fueled internal combustion (IC) engines.

In the last 10 years, two parallel development efforts related to lean-combustion vehicles have taken place: (a) “lean-burn” IC Otto cycle engines and (b) emission after-treatment for such engines and for diesel engines. The long-term viability of lean-burn engines depends on the development of successful (i.e. active and durable) systems. The main difficulty is to devise a reliable method to remove the oxides of nitrogen from an exhaust stream containing a large excess of oxygen. Diesel exhaust carries an added burden of controlling the soot particles which form in compression–ignition engines.

Short of NO decomposition, which has repeatedly been shown to be impractical under automotive conditions, there are only two possible ways of NO_x removal in the presence of excess oxygen: (a) selective catalysis in which a reductant, present in the exhaust or deliberately added to it, is oxidized solely or preferentially by the oxygen from the NO_x [33]; (b) storage of NO_x for a period of lean operation followed by a short-duration catalytic, reductive purging of the stored nitrogen oxides as N_2 [34]. The latter is a partial lean-burn strategy since an occasional brief operation under rich conditions is required to remove the stored NO_x. As is immediately apparent, the flow-through, continuous selective catalytic reduction (SCR) is the simpler and preferred route if an active enough catalyst can be found which selectively reacts the residual HC with the NO to produce dinitrogen. On most catalysts, including the widely researched zeolites containing active exchanged or deposited species, the selectivity is not as yet nearly adequate [33]. This calls for addition of hydrocarbon reductants, resulting in a system which is much less passive with respect to the involvement of the vehicle user. Another hindrance is the low durability of zeolite catalysts which are vulnerable to hydrothermal attack at elevated temperatures [35]. There have been several attempts to improve the hydrothermal stability of zeolitic SCR catalysts, mainly by the incorporation of alkaline earth and rare earth metal ions [36]. The issue of poisoning of the non-noble metal active sites by sulfur and phosphorus in the exhaust and by the water vapor itself is also not resolved completely. Notwithstanding the virtual deluge of publications and announcements of catalysts deemed suitable for practical application, the penetration of NO_x SCR into practice has been slow. Coupled with this, the penetration of “lean-burn” Otto cycle powertrains has therefore also been slow.

Efforts in NO_x aftertreatment of diesel exhaust have coalesced, in addition to devising an SCR system based on HC (including diesel fuel itself) as reductants, on the SCR process now widely used in the treatment of emissions from stationary sources, namely using N-containing reductants which reduce NO_x with a much better selectivity than that obtainable with HC. This will require careful dosing of the reductant (either ammonia or an aqueous solution of urea) with the aim to titrate essentially quantitatively the NO_x of the diesel exhaust. This approach will inherently be more complex than a simple, passive exhaust catalyst.

The trapping of NO_x during lean operation coupled with periodic purging is illustrated by reference [34]. The material in the trap storing the NO_x is usually a basic oxide which adsorbs the acidic oxides of nitrogen. For our purposes, we take BaO as a representative adsorbent since it is the material considered for practice in most cases. It adsorbs NO_2 much more efficiently than NO and therefore catalytic Pt particles which promote oxidation of NO are incorporated. This catalyst also promotes the oxidation of SO_2 to SO_3, the latter also being strongly adsorbed by BaO. Because the thermodynamic stability of surface sulfates is considerably higher than that of surface nitrates, the sulfates are not decomposed during purging cycles and thus deactivate the adsorbent. Moreover, there is another weakly acidic gaseous molecule in the exhaust at concentrations several orders of magnitude above that of NO_x, namely CO_2. This causes the bulk of the Ba in the trap to be present as carbonate with only the surface layers being used in the trapping of the NO_x. The catalytically active Pt plays an important role during the periodic regeneration of the trap when it promotes the reduction of the trapped NO_x to nitrogen.

Because of the stability of surface sulfates, it is difficult to regenerate a poisoned trap. High temperatures are required and these have to be induced by combustion heat generated from fuel-rich engine operation, this being coupled with secondary air injection. The implementation of NO_x trapping systems will be dependent on very low sulfur content in the fuel, as is presently the case in Japan (Fig. 9) [37]. As to the future of catalytic research in this area, it has to address another selectivity issue, namely a search for catalysts

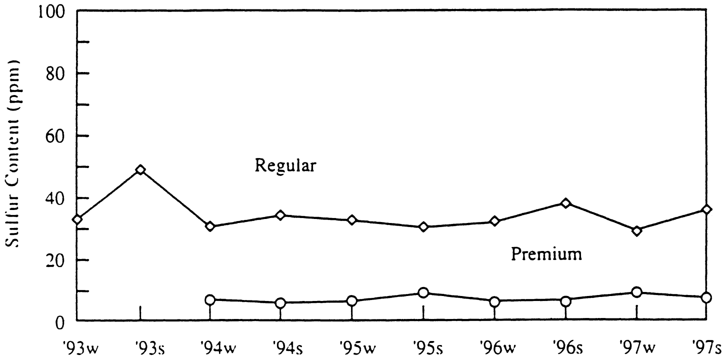

Fig. 9. Trends in sulfur content (ppm) of regular and premium Japanese gasolines (from Ref. [37]).

active in the oxidation of NO to NO_2 and relatively inactive in the oxidation of SO_2 to SO_3.

Yet another catalytic challenge associated with lean burn vehicles is control of particulate emissions, primarily for diesel vehicles but also of potential concern for direct-injection gasoline vehicles. Two broad applications of catalysis are currently being pursued in this regard. The first is catalytic soot combustion, either via a fuel additive or via a catalyzed filter or by combining both approaches [38–40]. In both cases, soot is usually collected on a wall-flow monolith filter which consists of alternately plugged and open channels requiring the exhaust gases to enter in one channel and flow through the porous cell wall (depositing soot on the cell wall) and out the adjacent channel. Collecting the soot is the relatively easy part of the cycle; burning off the collected soot in a controlled fashion and at the low operating temperatures of diesel exhaust is the harder task. Without a catalyst, soot combustion occurs ca. 500°C, far above the normal operating range of diesel vehicles. With the assistance of catalysts, either supplied continuously at low levels as a fuel additive (notably cerium but also others) or applied directly to the diesel particulate filter, the regeneration temperatures can be the region of 350°C. Since the catalytic additives which promote the combustion of the soot are themselves emitted into the atmosphere, they must be environmentally harmless.

The second broad application of catalysis for diesel particulate control is the continuously regenerable trap (CRT), conceived by Johnson Matthey [41]. The CRT utilizes an oxidation catalyst upstream of a conventional wall-flow diesel particulate filter. The oxidation catalyst serves to oxidize the volatile organic fraction of the soot mass and, more importantly, convert NO to NO_2. The NO_2 then promotes combustion of the collected soot at rates much greater than obtainable with O_2, thereby decreasing regeneration temperatures to ca. 300°C and enabling a more or less continuous conversion of soot.

At this time, all of the above approaches still need substantial development to be viable for broad commercial use. The relatively high soot ignition temperatures associated with the fuel additive or directly catalyzed particulate filters often lead to excessive buildup of soot prior to ignition, thereby resulting in temperature runaways and melting/cracking of the filter in some cases. The CRT, although more easily controlled, has the serious limitation that the oxidation catalysts developed thus far all suffer from severe poisoning of the NO to NO_2 reaction by fuel sulfur. For good conversion of NO to NO_2 diesel fuel is required which is almost sulfur-free (ca. 10 ppm S), and such clean diesel fuel is only available in a few European countries at the present time. Finally, it should be noted that the combined demands of particulate control and NO_x conversion can lead to quite complicated and large aftertreatment systems on diesel vehicles. One scenario would consist of an oxidation catalyst followed by a particulate filter, followed by a urea injection system and an SCR catalyst, followed by yet another oxidation catalyst to convert any slip of ammonia. Packaging and the ability to achieve temperatures required for the various catalytic reactions are still major question marks at the present time.

Finally, we note that there is also an effort to utilize non-thermal plasma technology as an aid in the catalytic treating of emissions from lean-burn engines.

8. Automotive catalysts “upstream” of the power plant

The accumulation of CO_2 in the atmosphere from the burning of fossil fuels, possibly associated with climate change, has moved to the forefront of international environmental concerns. Among the schemes to mitigate the contributions of vehicular transport to the accumulation of CO_2 in the atmosphere, the most radical one is to move completely away from fossil fuels to hydrogen, ideally derived from solar energy (and water) either by photovoltaics or through the harvesting of biomass with contributions from hydropower and nuclear energy. As the era of affordable and abundant solar energy is still a distant promise, it is proposed in the interim to draw primary energy for hydrogen production from fossil fuels, chiefly natural gas. The power plant of the highest theoretical promise is the fuel cell in which the chemical energy of the hydrogen is converted to electricity with an efficiency exceeding that achievable from a Carnot-cycle thermal engine such as used today. Owing to the very low volumetric energy density of hydrogen, the distribution and on-vehicle storage pose high practical hurdles to its use. To overcome this drawback, it is proposed, in turn, to convert on-board a liquid such as methanol, derived from the natural gas primary fuel, to the hydrogen required by the fuel cell power plant. The idea of on-board methanol reforming goes back at least to the mid 1970s [42]. There are also competing proposals to use the widely available gasoline for the on-board conversion. This approach will obviate the need for a new fuel whose present production is far below that of gasoline and for a new distribution system. All reforming processes are, of course, catalytic; and from a technical standpoint, the reforming of gasoline (HC) is more demanding than that of methanol.

We consider briefly the prospective involvement of on-board catalysis for chemical processing upstream of the fuel cell power plant instead of cleaning the exhaust. While the fuel cell itself is also a catalytic, or more precisely, an electrocatalytic, device using noble metals as catalysts, we will confine the discussion to the on-board fuel reforming catalytic processes and to the use of methanol as the hydrogen “carrier” since the conversion of methanol is considerably simpler than that of other liquid fuels. Anticipating business opportunities, several companies have entered this field at the R&D and demonstration levels. Among these are Johnson Matthey, Arthur D. Little/Epyx, Haldor Topsoe, Wellman CJB, Catalytica and several others. In-house investigations are being carried out at several automotive and energy companies and there is also much academic research.

Reforming a hydrocarbon fuel, whether oxygenated or not, requires breaking the chemical bonds in the fuel and making CO (and CO_2) and H_2 molecules from it (catalytic process A, endothermic). Further, it requires shifting over the CO further into CO_2 and additional hydrogen by reacting it with water (catalytic process B, slightly exothermic). The CO_2 is rejected into the atmosphere while the hydrogen is fed to the anode of the fuel cell after deep purification from residual CO (catalytic process C, slightly exothermic). There are hence two catalytic processes, endothermic and exothermic, in series, in addition to the electrocatalytic process of the fuel cell itself. All operate at variable loads dictated by the power demand of the vehicle. One of the main challenges is supplying the heat to drive the endothermic steam reforming reaction. Currently this is being approached in two ways: (1) introduction of air along with the fuel and water to effect a partial oxidation of the fuel (POX) thus providing heat for the steam reforming reaction which occurs simultaneously and (2) burning some of the fuel (or tail gases) directly and transferring heat by a heat exchanger to the steam reformer. In some embodiments partial combustion, reforming and water gas shift steps are combined in so-called “autothermal” reactors. The various approaches have pros and cons which are beyond the scope of this review and the reader is referred to recent publications [43–46] for more information.

Considering the above, it is fair to state that the proposed “upstream” catalytic system is immensely more complicated and more difficult to package on-board and implement in practice compared with the post-combustion, essentially passive, catalytic exhaust treatment. However, the most important difference between the “upstream” fuel-reforming and catalytic aftertreatment, not often articulated, is the dependence of the functional reliability of the vehicle on the *flawless* performance of the fuel reforming system. Any disturbance or malfunction in the fuel reforming process is likely to disable the vehicle or at least seriously impair its performance. Conversely, an occasional disturbance or malfunction in the operation of a downstream catalyst does not affect the operability of the vehicle and the vehicle operator becomes aware of the problem only if the vehicle is equipped with on-board diagnostics mentioned above. Even if the feasibility of on-board reforming were to be demonstrated in prototypes, to reach the required reliability for a 10-year in-use period with minimal maintenance represents a formidable challenge unprecedented in previous experience with stationary catalytic installations.

The issue of noble metal usage in the context of on-board fuel reforming coupled to the fuel cell is also worth pondering. For a long time, one of the main inhibitors of considering proton exchange membrane (PEM) fuel cells for automotive use was the excessive demand for the Pt to be used in the fuel cell electrodes. In the late 1980s and early 1990s, this demand was lowered by more than an order of magnitude. Nevertheless, it still requires about 1–2 g Pt/kW which, for a vehicle having a rated power of 50 kW, will add up to 50–100 g of Pt per vehicle. One cannot at this time accurately estimate the anticipated noble metal use for the “upstream” catalytic installation. The industrial practice for natural gas reforming and water–gas-shift does not employ noble metal catalysts but the faster rates demanded by the space-limited on-board installations will surely call for noble metals in the reforming reactors. A back of the envelope conservative estimate based on the data in various papers gives a ballpark figure of 0.5 g Pt/kW (25 g Pt for a 50 kW rated vehicle). Preferential oxidation of residual CO in H_2-rich streams (PROX) is also based on Pt (and other precious metal active elements) catalysts. Gasteiger and coworkers [47,48] did estimate the required amount of Pt + Au as 0.3 g/kW (15 g PM for a 50 kW rated vehicle). The alternative means for purifying the hydrogen from residual CO, based on H-permeation through Pd membranes, will require appreciable quantities of the latter metal. Adding together the noble metals to be used in a fuel cell vehicle with an on-board fuel reforming train, we come up with a conservative ball-park number of 100–150 g. For comparison, the present use in exhaust treatment is 2–5 g per vehicle with engines whose rated power considerably exceeds 50 kW. It is therefore, safe to assume that an important fraction of future research efforts will be devoted to the optimal utilization of noble metals. We may recall that the concern of the availability of sufficient sources of noble metals also antedated the catalytic treatment of auto emissions. This did not turn out to be a show stopper after all. In the case of on-board fuel reforming, the requirements of noble metals appear, as of now, to be much higher.

It is instructive then to compare the expected technical hurdles in catalytic on-board fuel reforming with those of 25–30 years ago relating to exhaust catalysts discussed at the beginning of this article and it is fairly clear that the challenges differ not only in degree but are of a different kind altogether. The first test of long-term reliability of an (electro)catalytic system operating at constantly variable load in a vehicle will be that of the fuel-cell power plant itself. This activity is being pursued feverishly now and the technical viability of the vehicular fuel cell should become clear within five years or perhaps sooner. If the outcome is positive, both the commercial motivation and the successful example will stimulate redoubled efforts in on-board fuel conversion catalysis.

9. Future R&D in automotive catalysis

A while ago, before the amended Clean Air Act in 1990, the tightened regulations in California and Europe, and the Tokyo Climate Change agreement of 1996, it looked as if the whole field had reached so-called “technological maturity” and that this augured a slackening in R&D efforts. As described above, quite the contrary has actually happened and societal pressures have, if anything, accelerated the pace of research. The areas that will be pursued vigorously in the next decade are likely to be the following:

- selective catalysts for the reduction of oxides of nitrogen in excess of oxygen;
- selective catalysts for the oxidation of nitric oxide in the presence of sulfur dioxide;
- catalyzed adsorbent materials (i.e. traps) for both HC and NO_x;
- catalytic systems for the combustion of carbonaceous particulates;

- catalysts stable at ever-increasing exhaust temperatures;
- low-temperature "light-off" catalysts;
- active catalysts for fuel reforming resistant to poisoning by sulfur;
- low-temperature selective catalysts for oxidizing CO preferentially in a hydrogen-rich stream;
- fuel cell electrocatalysts less sensitive to poisoning by CO;
- electrocatalysts for direct methanol fuel cells.

One final point bears mentioning. Catalyst poisoning due to sulfur compounds derived from fuel sulfur presents a major challenge, intractable thus far, to development of many of the technologies listed above. Efforts to develop catalysts, "traps" or electrocatalysts that are "tolerant" of sulfur are continuing even while there is a growing trend to regulate fuel sulfur levels to lower and lower values. Whether sulfur-tolerant catalysts will eventually be found or whether the ultimate solution will lie in an essentially complete removal of sulfur from fuel is an issue that is also likely to be resolved over the next decade.

References

[1] M. Shelef, K. Otto, N.C. Otto, Adv. Catal. 27 (1978) 311.
[2] M. Shelef, Catal. Rev. Sci. Eng. 11 (1975) 1.
[3] J.T. Kummer, J. Prog. Energy Combust. Sci. 6 (1980) 177.
[4] J.T. Kummer, J. Phys. Chem. 90 (1986) 4747.
[5] K.C. Taylor, Catal. Rev. Sci. Eng. 35 (1993) 457.
[6] J.J. Mooney, Exhaust control, automotive, in: Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 9, 4th Edition, Wiley/Interscience, New York, 1994, p. 982.
[7] E.E. Weaver, J.W. Shiller, A.G. Piken, Performance of monolithic catalysts in a vehicle field test, AIChE Symp. Ser. 72 (156) (1976) 369.
[8] C. Meguerian, E. Hirschberg, F. Rakovsky, US Patent 4,006,103.
[9] K.C. Taylor, J.C. Schlatter, J. Catal. 63 (1980) 53.
[10] H. Muraki, H. Sobukawa, M. Kimura, A. Isogai, Society of Automotive Engineers Paper No. 900610 (1990).
[11] Y.-K. Lui, J.C. Dettling, Society of Automotive Engineers Paper No. 930249 (1993).
[12] J.C. Summers, W.B. Williamson, Paper Presented at the Seminar on Pt Group Metals, International Precious Metal Institute, Las Vegas, Nevada, January 29–31, 1989.
[13] H. Muraki, Society of Automotive Engineers Paper No. 910842 (1991).
[14] H. Muraki, H. Shinjoh, H. Sobukawa, K. Yokota, Y. Fujitani, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 202.
[15] H. Muraki, H. Sinjoh, Y. Fujitani, Appl. Catal. 22 (1986) 325.
[16] R.W. McCabe, R.K. Usmen, in: W.N. Delgass, E. Iglesia, A.T. Bell (Eds.), Studies in Surface Science and Catalysis, Vol. 101, Elsevier, Amsterdam, 1996, p. 355.
[17] D.R. Monroe, M.H. Krueger, D.D. Beck, M.J. D'Aniello Jr., in: A. Crucq (Ed.), Catalysis and Automotive Pollution Control II, Studies in Surface Science and Catalysis, Vol. 71, Elsevier, Amsterdam, 1991, p. 593.
[18] D.D. Beck, J.W. Sommers, C.L. DiMaggio, Appl. Catal. B 3 (1994) 205.
[19] P. Gross, W.F. Biller, D.F. Greene, K.K. Kearby, US Patent 3,370,914.
[20] E.M. Logothetis, R.E. Soltis, in: Proceedings of the Electrochemical Society 97-19 (Chemical and Biological Sensors and Analytical Electrochemical Methods), 1997, pp. 88–93.
[21] H.S. Gandhi, A.G. Piken, M. Shelef, R.G. Delosh, Society of Automotive Engineers Paper No. 760201 (1976).
[22] J.C. Summers, S.A. Ausen, J. Catal. 58 (1979) 131.
[23] A. Trovarelli, Catal. Rev. Sci. Eng. 38 (4) (1996) 439.
[24] G. Kim, Ind. Eng. Chem. Prod. Res. Dev. 21 (1982) 267.
[25] W.B. Williamson, J.C. Summers, J.F. Skowron, Society of Automotive Engineers Paper No. 880103 (1988).
[26] H.S. Gandhi, M. Shelef, Appl. Catal. 77 (1991) 175.
[27] R.K. Usmen, R.W. McCabe, G.W. Graham, W.H. Weber, C.R. Peters, H.S. Gandhi, Society of Automotive Engineers Paper No. 922336 (1992).
[28] M. Funabiki, T. Yamada, Society of Automotive Engineers Paper No. 881684 (1988).
[29] G.J.J. Bartley, P.J. Shady, M.J. D'Aniello Jr., G.R. Chandler, R.J. Brisley, D.E. Webster, Society of Automotive Engineers Paper No. 930076 (1993).
[30] J.-P. Cuif, S. Deutsch, M. Marczi, H.-W. Jen, G.W. Graham, W. Chun, R.W. McCabe, Society of Automotive Engineers Paper No. 980668 (1998).
[31] H.-W. Jen, G.W. Graham, W. Chun, R.W. McCabe, J.-P. Cuif, S.E. Deutsch, O. Touret, Catal. Today 50 (2) (1999) 309–328.
[32] M. Jacoby, Chem. Eng. News 77 (4) (1999) 36.
[33] M. Shelef, Chem. Rev. 95 (1995) 209.
[34] N. Takahashi, et al., in: C. Centi, S. Perathoner, C. Cristiani, P. Forzatti (Eds.), Proceedings of the First World Congress on Environmental Catalysis, Pisa, Italy, May 1–5, 1995, Societa Chimica Italiana, Rome, pp. 45–48.
[35] R.A. Grinsted, H.-W. Jen, C.N. Montreuil, M.J. Rokosz, M. Shelef, Zeolites 13 (1993) 602.
[36] M.J. Rokosz, A.V. Kucherov, H.-W. Jen, M. Shelef, Catal. Today 35 (1997) 65.
[37] H. Nomura, Proceedings of Agelfi — 13th European Automotive Symposium, Seville, Spain, September 24–25, 1998, p. 121.
[38] H. Luders, et al., Society of Automotive Engineers Paper No. 952493 (1995).
[39] H. Luders, R. Backes, P. Stommel, Society of Automotive Engineers Paper No. 970470 (1997).
[40] S.J. Jelles, et al., Society of Automotive Engineers Paper No. 1999-01-0113.
[41] B.J. Cooper, J.E. Thoss, Society of Automotive Engineers Paper No. 890404 (1989).

[42] L. Kester, A.J. Konopka, E.H. Camara, in: Proceedings of the 10th Rec. Intersoc. Energy Conf., 1975, pp. 1176–1183.
[43] S. Golunski, Plat. Met. Rev. 42 (1998) 2.
[44] J. Flynn, et al., Society of Automotive Engineers Paper No. 1999-01-0536 (1999).
[45] B. Hohlein, M. Boe, J. Bogild-Hansen, P. Brockerhoff, G. Colsman, B. Emonts, R. Menzer, E. Riedel, J. Power Sources 61 (1996) 143.
[46] B. Emonts, J. Bogild-Hansen, S. Loegsgaard Jorgensen, B. Hohlein, R. Peters, J. Power Sources 71 (1998) 288.
[47] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. Catal. 171 (1997) 93.
[48] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. New Mater. Electrochem. Syst. 1 (1998) 39.