ACADEMIC
PRESS

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Catalysis 216 (2003) 433–442

JOURNAL OF
CATALYSIS

www.elsevier.com/locate/jcat

Automotive exhaust catalysis

H.S. Gandhi, G.W. Graham, and R.W. McCabe *

Ford Motor Company, MD3179/SRL, PO Box 2053, Dearborn, MI 48121, USA

Received 24 July 2002; revised 5 September 2002; accepted 17 September 2002

Abstract

Research in the field of automotive exhaust catalysis has paralleled the broader growth in heterogeneous catalysis research—beginning in the 1960s, progressing through commercialization in the mid-1970s, and continuing today. The general trend has been one of increasingly complex catalyst formulations in response to increasingly stringent emission standards. Nowhere is this more evident than in the various means that have been employed to most effectively utilize the noble metal components. These efforts will continue, but with greater emphasis on optimizing catalyst formulations for lean-burn applications and reducing catalyst cost and complexity without sacrificing performance.

Keywords: Automative exhaust catalyst; TWC; Oxygen storage capacity; Platinum; Palladium; Rhodium; Ceria; Zirconia

1. Introduction

Commercial applications of catalytic pollution control from internal combustion engines were virtually nonexistent 40 years ago when the first volume of the *Journal of Catalysis* was published. Today, exhaust catalysts are found on nearly all US passenger cars, light- and medium-duty trucks, and even some heavy-duty trucks. Similar situations exist in Europe, Japan, and other regions with large populations of automobiles, and exhaust catalysis is rapidly being embraced in countries such as India and China where recent regulations providing for lead-free fuel have opened the door for catalytic emissions control. The history of catalytic exhaust gas after-treatment—the largest application of heterogeneous catalysis by many measures—is a complex one involving numerous players (automobile manufacturers, government agencies, catalyst suppliers, petroleum refiners, and fuel-additive suppliers, among others). Their contributions go far beyond advances in catalyst technology alone, and a number of detailed reviews have been published that cover the broad waterfront of automotive emissions control [1–9]. Distilled to its essence, however, the story of automotive exhaust catalysis revolves around three noble metals—platinum, palladium, and rhodium—that have been dispersed, stabilized, promoted, alloyed, and segregated in increasingly sophisticated ways over the years to achieve extraordinary advances in performance and durability. It is a story that parallels the tremendous growth in many areas of catalysis research and development over the past 40 years. In this paper, we focus on the major advances in utilization of these three metals and assess the challenges that remain.

2. Why Pt, Pd, and Rh?

Much of the early R&D on automotive catalysts, prior to commercialization in the 1975 time frame, was devoted to non-noble metal catalysts (so-called base metal catalysts), largely due to concerns over the cost and availability of noble metals. However, it quickly became apparent that the base metals (oxides of Ni, Cu, Co, Mn, and Cu/Cr, for example) lacked the intrinsic reactivity, durability, and poison resistance required for automotive applications [2–5,7]. Hence, research on noble metal catalysts began early on, in recognition of their excellent thermal stability, their lower tendency (compared to the base metals) to react with support materials, and their ability to process gas streams containing upwards of 1000 ppm (by weight) sulfur without being transformed to bulk sulfates.

Perhaps the most important factor culling the list of candidate platinum group metals was the recognition that Ru, Ir, and Os all form volatile oxides. Thus, Pt and Pd were left as clear choices for the oxidation catalysts employed during the first phase of catalytic emission controls beginning

---

[*] Corresponding author.
E-mail address: rmccabe@ford.com (R.W. McCabe).

0021-9517/03/$ – see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0021-9517(02)00067-2

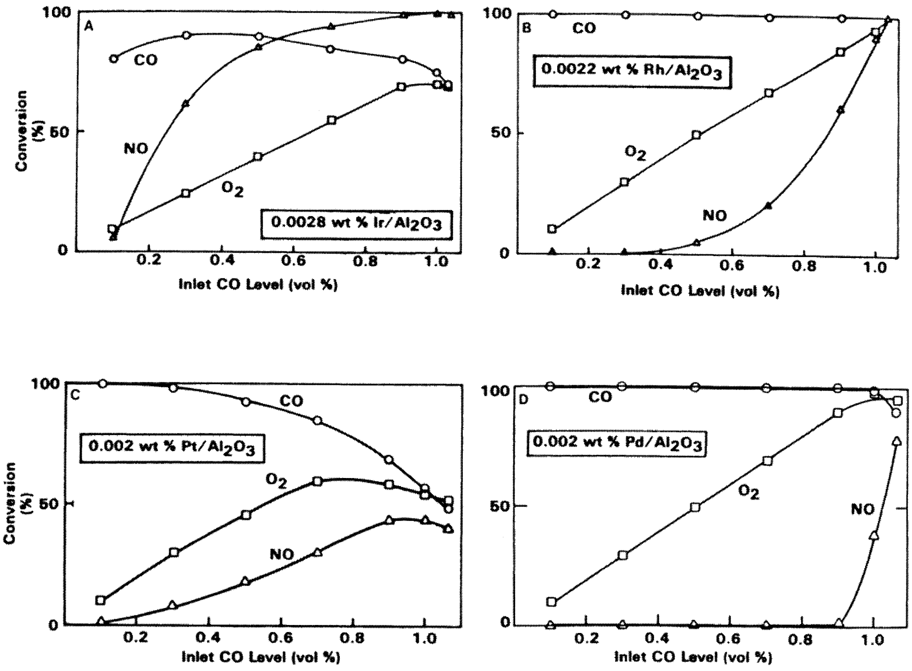

Fig. 1. Plot of NO, CO, and O_2 conversion over Ir, Rh, Pt, and Pd on alumina catalysts as a function of inlet level of CO (reproduced from [15] with permission from Elsevier Science). Feedstream composition: 0.05 vol% NO, 0.5 vol% O_2, 10 vol% H_2O, 0 to 1.05 vol% CO, and balance N_2. Catalyst temperature: 550 °C.

in the US in 1975, especially since Rh is scarce relative to Pt and Pd and exhibits lower activity for olefin conversion under oxidizing conditions [4]. The selection of a suitable NO_x reduction catalyst (required from late 1979 on) was not as obvious, however. The first catalyst systems for converting HC, CO, and NO_x employed a dual-bed converter in which NO_x was reduced in the first bed and CO and HC were oxidized in the second bed, utilizing secondary air injected between beds. Formation of NH_3 in the first bed could not be tolerated in a dual-bed converter arrangement because the NH_3 would be reconverted to NO_x in the second bed. Despite the volatility of its oxide, Ru was investigated thoroughly as a potential NO_x catalyst due to its relatively high selectivity toward N_2 rather than NH_3. A number of studies were carried out at Ford [10–12] and elsewhere [13,14] during the early to mid-1970s exploring the effectiveness of stabilizing Ru against volatilization by deploying it in the form of various pure ruthenate compounds ($MRuO_3$, where M = Ba, Sr, La) and also substituted ruthenates such as $LaNi_xRu_{1-x}O_3$ and $BaMn_xRu_{1-x}O_3$. Although impressive gains in stability were realized, they came at the expense of slightly reduced activity for NO reduction, and more importantly, significantly increased NH_3 selectivity. Thus, stabilizing Ru undid the key reason for considering it in the first place, and a Ru-based NO_x reduction catalyst never made it to production.

Rh became the catalytic element of choice for NO_x control. The reason is apparent from Fig. 1 comparing conversions of NO, CO, and O_2 over Ir, Rh, Pt, and Pd catalysts, all supported at roughly equivalent loadings on alumina [15]. Note that the extreme right-hand set of data points in each frame represents the stoichiometric condition. Thus, the critical measure of each element is its ability to achieve high NO_x conversion near stoichiometry and retain NO_x conversion into the "lean" regime (i.e., CO concentrations less than 1.05 vol% in Fig. 1) given the transient nature of automotive air–fuel control. Clearly, Rh fills these combined requirements best (excluding Ir for the volatility of its oxides) and, further, has lower selectivity for NH_3 production under rich conditions than the other noble metals in Fig. 1.

3. Early three-way catalysis

The move to stricter NO_x standards in the 1980 time frame, together with the limitations of dual-bed converter systems, spurred the development of feedback control technology that, by the mid-1980s, resulted in an industry-wide switch to three-way catalysis—so called because of the demands of simultaneously catalyzing three types of reactions: CO oxidation, hydrocarbon (i.e. HC) oxidation, and NO_x reduction. This approach remains the primary means of catalytic exhaust aftertreatment in practice today, but with significant advances over the years in three areas: catalyst technology, cold-start strategy, and air–fuel control hardware (and strategy). From the perspective of noble metal utilization, it is important to recognize that many of the advances in catalyst technology have come in response to advances in the other two areas, as well as changes in fuel chemistry. For example, the air–fuel perturbations imposed by the oxygen

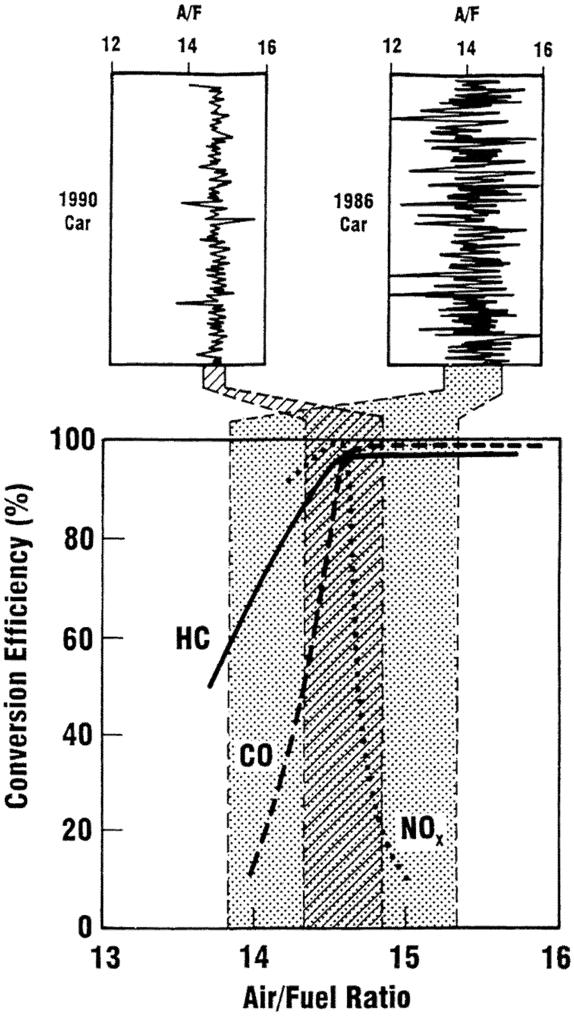

Fig. 2. Conversion efficiency vs air–fuel ratio (A/F) plot with typical air–fuel traces (showing actual variations in air–fuel ratio under closed-loop control) from 1986 and 1990 cars (reproduced from [8] with permission from Elsevier Science). The stoichiometric air–fuel ratio is about 14.7 (14.7 g of air for each gram of fuel).

feedback control sensor can be seen in Fig. 2 to result in significant deviation from ideal three-way operating conditions, particularly at the control levels typical of the mid-1980s. To compensate, oxygen storage components were added to the catalyst to buffer the impact of the perturbations on the catalyst. Nickel and iron oxides were used in some early formulations, but the industry quickly settled on ceria, which remains the oxygen storage component of choice in today's catalysts.

Early TWCs were relatively simple in formulation: for example, Pt and Rh dispersed at a weight ratio of 5:1 on an alumina-coated cordierite monolith (or alumina pellets) with ceria added for oxygen storage. Processing was kept simple to reduce cost, but resulted in little control over factors such as uniformity of metal distribution within the washcoat, extent of alloying or bimetallic particle formation between Pt and Rh, and distribution of the Pt and Rh between ceria and alumina as the supporting phase. Nevertheless, the formulations worked well with respect to the emission standards and mileage requirements in effect during the 1980s. Especially with the introduction of so-called Hi-Tech TWCs in the mid-1980s, which utilized high concentrations of high-surface-area ceria and stabilized aluminas (containing Ba or La), the general viewpoint in the industry was that TWC technology was mature and future reductions in emissions would likely come in the form of improvements in air–fuel control and cold-start strategies.

Pd, despite its low cost and broader availability relative to Pt, did not figure prominently in the TWC formulations of the 1980s, largely because of poisoning associated with lead (Pb) and sulfur. Pd is less noble than Pt, and thus more prone to interact with poison species. Gandhi et al. [16], for example, studied the affinity of lead for Pt, Pd, and Rh, deposited as sputtered films on various catalyst supports, and found that Pd was unique among the three metals in its tendency to form solid solutions with Pb (Fig. 3). Pt, in contrast, did not react directly with the Pb, but catalyzed its reaction with SO_2 (SO_3) to form relatively inert $PbSO_4$. Similarly, SO_2 poisoning of Pd is more severe than that of Pt owing to the tendency of Pd to incorporate S into the bulk under inert or reducing conditions, with subsequent removal requiring high-temperature treatment [17]. In general, the poisoning of automotive catalysts by sulfur is a complex phenomenon, involving both the noble metals and other washcoat components, and differing greatly in impact depending on the particular reaction and operating conditions such as temperature and exhaust gas composition. Detailed reviews have been published by Gandhi and Shelef [18] and Truex [17].

4. Rh-support interactions

One of the main challenges in the early TWCs, and indeed, one that persists today, is how to most effectively support Rh. Rh undergoes a strong deactivating interaction with alumina at temperatures ca. 600 °C and above [19,20]. Fig. 4, for example, shows the loss in Rh reducibility that accompanies aging of a 0.5% $Rh/\gamma\text{-}Al_2O_3$ catalyst at successively higher temperatures [21]. Most of the reducibility (as measured by temperature-programmed reduction) is lost after 1 h oxidation at 700 °C, but can be almost totally restored by reduction at 800 °C. A number of explanations have been proposed for the nature of the high-temperature oxidizing interaction including rhodium aluminate formation [22], dissolution of Rh into the alumina [19,21,23], encapsulation of the Rh by the alumina [23,24], and spreading and interaction of Rh oxide over the alumina support surface [25]. Although the mechanism is still unresolved, the strategy for avoiding the deleterious interaction between Rh and alumina has been to seek alternative supports. Ideally, Rh should be supported on ceria for best CO and NO_x performance, and one of the reasons the High-Tech TWCs of the mid-to-late 1980s employed high loadings of ceria—sometimes up to 50% of the

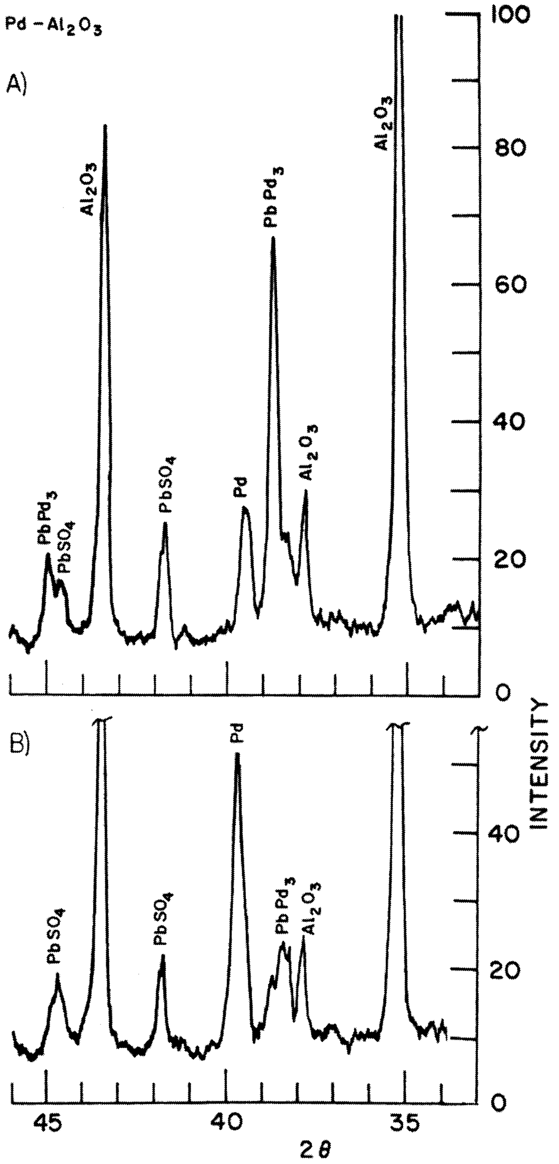

Fig. 3. X-ray diffraction traces of Pd/Al_2O_3 catalyst after exposure to Pb for 72 h at 700 °C (A) and following subsequent oxidation in air at 700 °C (B) (from [16]). Exposures were performed in a pulsed-flame combustor burning isooctane doped with 1.5 g Pb (derived from tetraethyllead) per gallon and 0.03 wt% S (derived from diethyl sulfide).

washcoat composition—was to maximize the likelihood of Rh particles ending up in contact with ceria rather than alumina. However, Rh also deactivates by forming rare earth rhodate species in oxidizing environments, and cerium rhodate, in particular, resists reduction at temperatures up to 450 °C [26]. Yao and co-workers [20] showed that Rh on both α-Al_2O_3 and ZrO_2 can be oxidized at temperatures up to 900 °C while still retaining substantial CO adsorption capacity, in contrast to Rh on γ-Al_2O_3 (Fig. 5). Thus, the trend in recent years has been to support Rh on oxides other than γ-Al_2O_3, and in the case where ceria is used, to employ mixed oxides of ceria and zirconia [27].

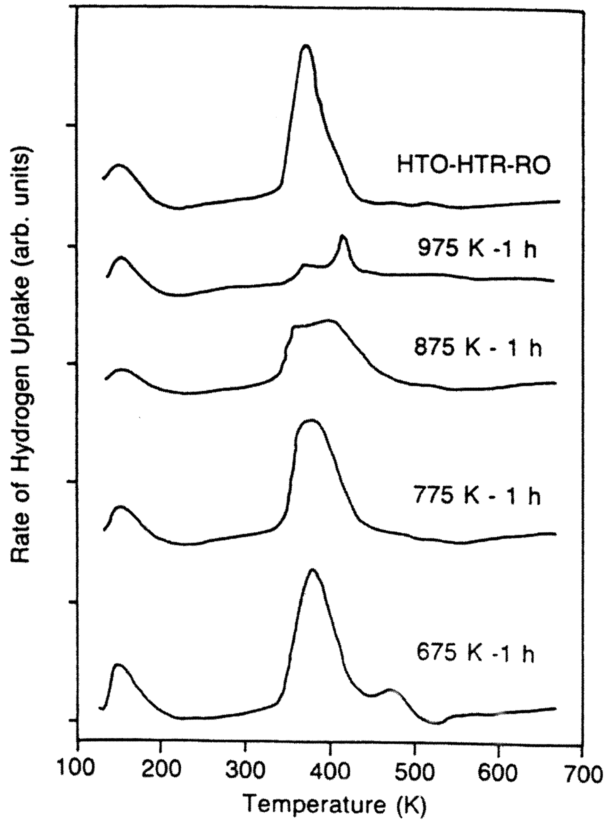

Fig. 4. Temperature-programmed reduction profiles for 0.5% Rh/γ-Al_2O_3 after 1-h oxidation treatments at different temperatures (reproduced from [21] with permission from Elsevier Science). The profile labeled HTO–HTR–RO was obtained after regeneration, performed by heating the sample that had been oxidized at 1075 K (HTO) in 5% H_2 at 1075 K (HTR), followed by heating in 5% O_2 at 775 K (RO).

5. The emergence of Pd

Steady decreases in the concentration of residual lead in US unleaded fuel throughout the 1980s resulted by the end of the decade in levels less than 0.001 g/gal and negligible effect on Pd performance under three-way conditions. This opened the door for partial substitution of Pt by Pd, and in early 1989, Ford introduced Pd/Rh catalyst technology in the California market. From a catalyst formulation standpoint, the introduction of Pd was significant in that it introduced a level of complexity largely absent in previous formulations. Specifically, Pd segregates as PdO on the

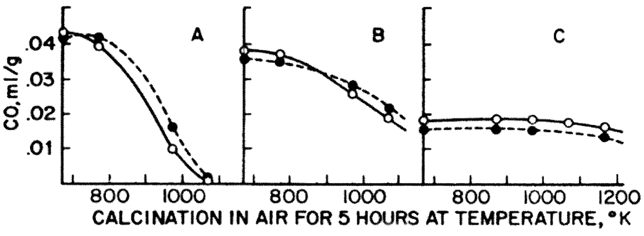

Fig. 5. CO chemisorption on Rh on various supports (reproduced from [20] with permission from Elsevier Science). (A) γ-Al_2O_3, (B) α-Al_2O_3, and (C) ZrO_2.

surface of Pd/Rh alloys (typical of automotive concentration ratios) under oxidizing conditions up to temperatures ca. 1000 K where PdO decomposes [28]. The surface segregation of Pd results in strong suppression of NO_x conversion in TWC applications where Rh is called on to carry on most of the NO_x reduction activity [29,30]. Thus, the Pd/Rh formulations brought the first real need to segregate the noble metals on different support particles. This, in turn, added considerable processing complexity to automotive catalysts, since it demanded either multiple coating passes (with calcination in between) or methods of "fixing" the noble metals onto separate support phases while in the slurry state. On the other hand, the new processing techniques opened the door for more highly engineered products that could take advantage of research discoveries made during the late 1970s and early 1980s. For example, studies at Ford [31] showed the tendency of noble metals to deposit in a highly dispersed state up to a threshold loading characteristic of the particular support and then, at higher loadings, to nucleate into larger particles with bulk-metal characteristics. Not only did this provide guidelines for the optimum loading of noble metals, but it allowed, within one catalyst formulation, the possibility of having both a dispersed metal phase (for structure-insensitive reactions) and an agglomerated metal phase (for structure-sensitive reactions such as alkane oxidation).

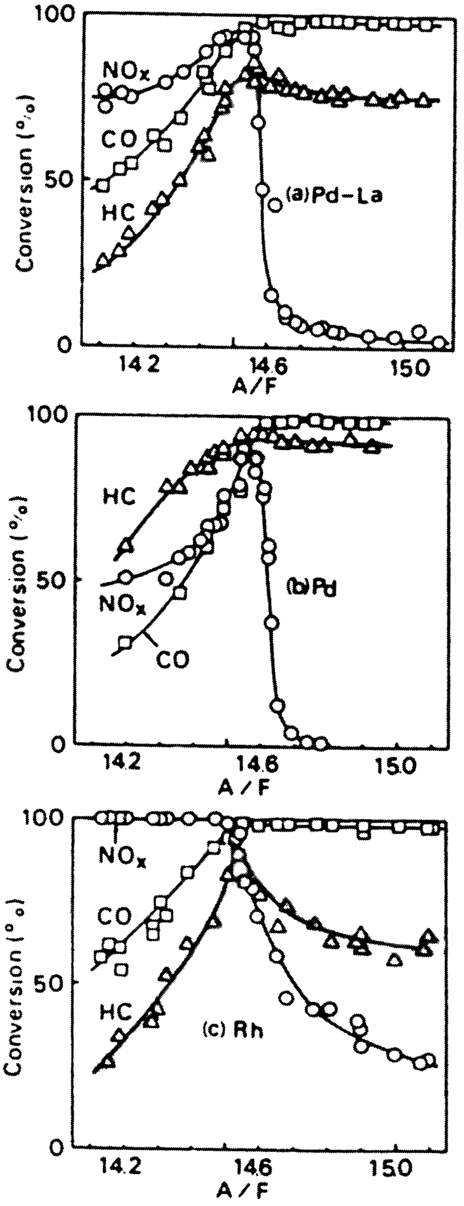

Fig. 6. Conversion efficiencies as a function of A/F of engine exhaust gas for (a) Pd–La, (b) Pd, and (c) Rh catalysts (reproduced from [35] with permission from Elsevier Science).

Although the Pd/Rh TWCs were the only Pd-containing TWCs to achieve commercialization during the 1980s, considerable research was invested in exploring the potential of Pd as substitute NO_x catalyst for the more expensive Rh. As noted above, early work at Ford [32] noted the possibility of using Pd with clean fuels containing little or no Pb and low levels of sulfur. Also, both Pt–MoO_3–Al_2O_3 [33] and Pd–WO_3–Al_2O_3 [34] catalyst formulations were investigated as substitutes for Rh-containing NO_x catalysts and found to have excellent N_2 selectivity. The MoO_3 catalyst showed NO_x reduction activity nearly as good as Rh; nevertheless, neither was commercialized due to problems with high-temperature volatilization of the MoO_3 as well as a tendency of the MoO_3 to react with alumina at elevated temperatures to form aluminum molybdate. Subsequent work by Muraki and co-workers at Toyota showed the potential for using Pd as a NO_x reduction catalyst, especially when promoted by La [35–37], as can be seen in Fig. 6. Note, however, the narrowness of the NO_x window for the Pd and Pd–La formulations compared to that for Rh (i.e., NO_x conversion drops more rapidly on both the rich and lean sides of the stoichiometric ratio near 14.6). Muraki et al. [36] offered various suggestions for the promoting influence of La and concluded that its main effect was to decrease the inhibition of NO_x reduction by hydrocarbons. Thus, the research of the 1980s showed that Pd had potential as a substitute for Rh in TWCs, but needed additional development prior to commercialization.

6. Advanced TWC formulations

The early 1990s brought a new wave of emission regulations to both the US and Europe. In California, especially, a series of low-emission vehicle (LEV) standards were enacted which started the progression toward a 10-fold reduction in HC emissions and 20-fold reduction in NO_x from levels prior to 1990. Conversion of hydrocarbons during the period immediately following cold start was quickly recognized as the chief challenge presented by the new standards. Initially, the strictest standards were expected to require new technology for converting or storing HC under cold-start conditions. Hydrocarbon trapping systems (zeolite based), electrically heated catalysts, and exhaust gas burner systems were all investigated [38]. However, most manufacturers soon realized that extremely fast light-off of the catalytic converter could be achieved through a combination of modified combustion strategy and fast light-off catalysts (either mounted close to the engine exhaust manifold or downstream with insulated exhaust pipes).

Along with the new emission standards of the early 1990s, new durability requirements were enacted. Useful life requirements were increased from 50,000 to 100,000 miles (120,000 miles for light-duty trucks). In addition, both federal and California regulatory agencies began to place more emphasis on emission audits of in-use vehicles rather than prescribed driving cycles, thus discovering that the approved durability driving cycles at the time were not as severe as typical field aging. These factors, combined with the higher operating temperatures of the fast light-off catalyst systems, revealed inadequate thermal durability of the catalyst formulations typical of the late 1980s and early 1990s. The shortcomings were manifested in "breakthrough" emissions of CO and NO_x (and sometimes HC) during transient driving modes (accelerations and decelerations) and could be traced to loss of oxygen storage capacity (OSC) with time in service. Post-mortem analyses of catalysts from the field showed that deactivation was linked to the "shotgun" method by which most of the catalysts were made. Most formulations still utilized one-step processing in which salts of both cerium and the noble metals were impregnated simultaneously onto alumina with the expectation that a substantial fraction of the noble metal would end up in contact with ceria. While this was true in the fresh catalyst, thermal aging promoted growth of both the noble metal and ceria particles with loss of contact area between the two. For example, analysis of a 50,000-mile-aged Pt/Rh catalyst from a 1990 Crown Victoria vehicle in our laboratory showed that the mean Pt particle size increased from 1.2–1.6 nm (fresh) to 11 ± 2 nm (aged), while the ceria particle size increased from about 9 nm (fresh) to 18 nm (aged) [39]. Moreover, TPR analysis showed the growth of high-temperature features characteristic of pure ceria in the aged sample versus low-temperature features associated with the noble metals in contact with ceria in the fresh sample.

Clearly, advances were needed in two areas—light-off performance and thermally stable oxygen storage components. Fortunately, breakthroughs occurred in both, although at the requirement of much more complex and sophisticated catalytic materials and formulation strategies than employed in the past. Considering the light-off issue first, research on Pd as an alternative to Pt/Rh for NO_x control had shown that excellent NO_x reduction could be achieved with Pd formulations when suitably promoted (as noted above) and when deployed at loadings higher than those for Pt/Rh [40,41]. Simultaneously, it was recognized that segregating a portion of the Pd from ceria produced better low-temperature performance (including light-off) [42]. This led to a trend quickly adopted by all of the major catalyst suppliers—deploying the noble metals in different layers or on different support particles within a single washcoat layer, not just to avoid deleterious metal–metal or metal–support interactions, but to optimize specific functions demanded of the catalyst. Fig. 7 shows an example of a layered washcoat structure. In this case, the view taken into the corner of a single

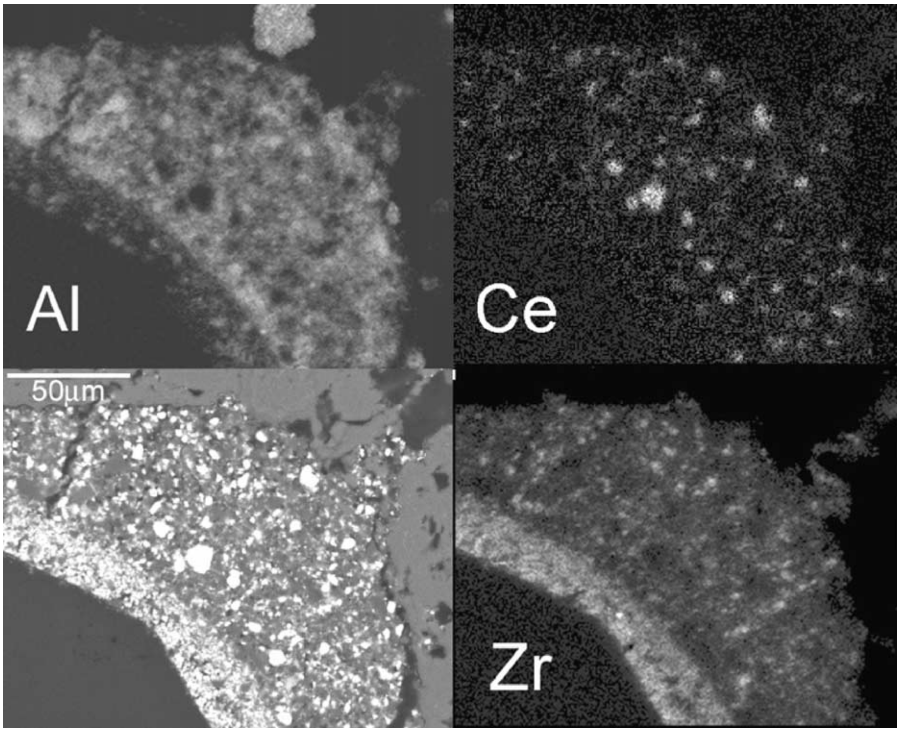

Fig. 7. Typical layered washcoat structure of current TWC (reproduced from [45] with permission from Imperial College Press). The lower left-hand panel is a backscattered electron image, and the other panels are chemical maps obtained with an electron microprobe.

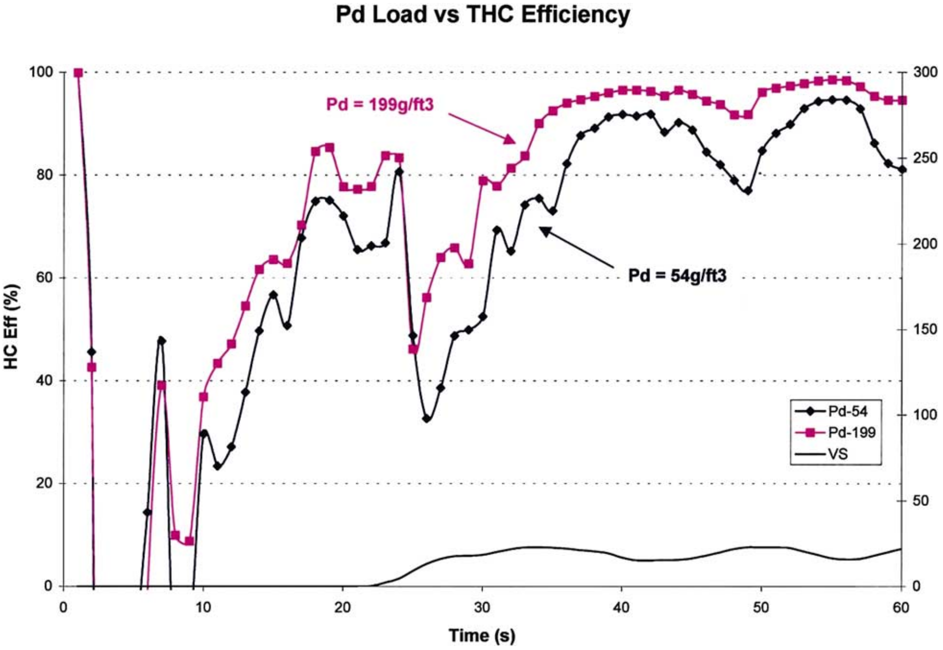

Fig. 8. Cumulative HC plot showing fast light-off during the first 60 s of the federal test procedure for two Pd catalysts with different Pd concentrations (loadings) (from Carolyn Hubbard). The axis on the right side of the graph is for the vehicle speed (VS) and has units of miles per hour.

channel of the monolith shows an alumina-rich underlayer and a ceria–zirconia overlayer. Reference [9] gives examples of layered washcoat strategies that have been used for trimetal (Pt/Pd/Rh) and Pd catalyst formulations. The Pd formulations demonstrate extremely good light-off performance. Fig. 8, for example, compares the HC conversion vs time profiles for 199 g/ft^3 and 54 g/ft^3 light-off catalysts on an Expedition vehicle during the federal test procedure. Both catalysts light off quickly, reaching 50% conversion between 13 and 15 s following cold start. However, the higher-loaded catalyst maintains significantly higher conversions, which translates into substantially lower cumulative emissions after 60 s (0.52 g) than obtained with the lower-loaded catalyst (0.77 g).

As noted above, fast light-off was one of two advances required by the emissions and durability requirements of the 1990s. The other was improved oxygen storage materials. Here the breakthrough came from the development of new “stabilized” cerias that not only provided better surface area stability after high-temperature aging, but more importantly, promoted oxygen transport from within the bulk rather than from the surface only. The best results thus far have been obtained with solid solutions of ceria and zirconia [43,44]. Table 1 shows the dramatic improvement in oxygen storage obtained for a model catalyst of 2%Pd on a 70wt%ceria–30wt%zirconia solid solution support (Pd/CZ3) compared to its counterpart on pure ceria (Pd/C2) [45]. Especially after “redox” aging at 1050 °C for 12 h, the ceria–zirconia-supported Pd retains anywhere from 12 to 30 times more OSC than the pure-ceria-supported Pd. Much effort has gone into studying the underlying basis for the improved oxygen storage associated with the mixed oxide support materials [45]. It is generally agreed that incorporating zirconia into ceria produces defects that greatly enhance the transport of oxygen from the bulk to the surface of the particle under reducing conditions, even though the defects are not readily observed by conventional analysis techniques such as X-ray diffraction. The transport of oxygen from deep in the bulk is evidenced from electron energy loss spectroscopy (EELS) of a model planar catalyst consisting of Pd particles supported on a single-crystal film of ceria–zirconia, as shown in Fig. 9 [46]. The peak ratio of the Ce M5 and M4 lines are characteristic of Ce^{4+} in the case of the oxidized film, as expected, regardless of whether the analysis is made at the surface of the film or at the interface between the ceria–zirconia and its underlying support (yttria-stabilized zirconia single crystal). After reduction, in contrast, the peak ratio shifts to that characteristic of mostly Ce^{3+} at the surface of the film, and even shows some evidence of ceria reduction extending down to the interface with the underlying support, a depth of 50 nm. Not only did introduction of the “stabilized” cerias greatly increase the thermal durability of the catalyst, but it also greatly enhanced the effectiveness of Pd by solving the

Table 1
Steady-state oxygen storage capacities of fresh and “redox” aged model Pd automotive catalysts made with ceria and ceria–zirconia [45]

Catalyst	CeO_2 (wt%)	State	Oxygen storage capacity (μmol O/g)		
			350 °C	500 °C	700 °C
Pd/C2	100	fresh	270	360	370
		aged	20	30	80
Pd/CZ3	70	fresh	890	970	1030
		aged	630	810	1070

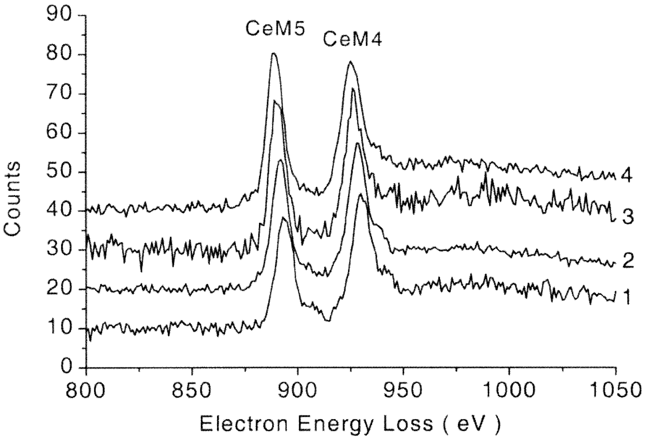

Fig. 9. EELS spectra of Ce acquired from the ceria–zirconia/yttria-stabilized zirconia interface (1, 3) and the ceria–zirconia film surface (2, 4) of a model planar catalyst sample before (1, 2) and after (3, 4) reducing treatment (reproduced from [46] with permission from the Microscopy Society of America).

problems of the narrow A/F operating window inherent in the early Pd-only formulations.

7. Future perspective

The advanced TWC formulations developed during the 1990s, with subtle modifications, are representative of the TWCs in use today. Typical catalysts are those that contain multiple noble metals supported on different phases with various stabilizers and additives to ensure high performance and durability. As with most technological developments in the auto industry, the first attempts to achieve the extremely stringent emissions requirements of the 1990s and beyond, were met with relatively complex and expensive catalyst technology. Some of the catalyst formulations are quite complicated and can contain up to three noble metals, three or four support phases, Ni as an H_2S storage agent, and four or five additional promoters and stabilizers. Given the high temperatures and wide-ranging exhaust compositions that are experienced over the life of the vehicle, this complexity can lead to multitude of solid-state reactions between the various components of the catalysts. Fig. 10, for example, shows a $Ni_xAl_2O_{3+x}$ ($x \leqslant 1$) nanotube (N) attached to a Pd particle at one end and a larger crystal of $Ni_xAl_2O_{3+x}$ at the other end [47]. This structure was observed by transmission electron microscopy (TEM) during analysis of a Pd-only catalyst that had been aged on an engine dynamometer for 120 h under a cycle that simulates 100,000 miles in the field. Nickel oxide is incorporated into the catalyst as an H_2S scavenger, but it somehow underwent reaction with alumina (present either as a support phase or binder material) at the Pd particle to form the observed structure during aging. Clearly, this morphology does not reflect the intended metal–support combination.

Another, though less dramatic, example of exposure to high temperature is illustrated in Fig. 11 [48]. The Pd–Rh alloy particle shown in this TEM micrograph formed as a result of the transport of the pure metals, initially loaded onto distinct support phases in a model bimetallic catalyst, over distances of order 10 µm (from one support particle to another) during 12 h of laboratory redox-aging at 1050 °C. Careful analysis of the alloy particle by energy dispersive X-ray spectroscopy (EDS) shows that its surface is enriched in Pd, which is undesirable due to a loss in NO_x performance. The avoidance of alloy formation in this case can only be accomplished by segregating the noble metals axially along the monolith, a recently implemented practice known as zone coating. Though more complex in terms of processing, this advance in washcoat technology can allow for greater flexibility in the design of catalyst systems. Further, zone coating, like the serial arrangement of discrete bricks, is beginning to lead to more efficient use of the noble metals. For example, high metal loadings, needed for close-coupled catalyst operation in order to maintain sufficient metal surface area at the low metal dispersions obtained (and desired for best light-off performance) due to severe particle coarsening, are applied in a short front zone. Much lower metal loadings (as little as 1/10), which suffice for downstream operation where higher metal dispersions can be maintained due to the lower temperatures, are applied in a longer rear zone. Future catalyst development will undoubtedly refine such a distributed approach in order to further optimize noble metal utilization.

The efficient use of noble metals looms as a challenge in an emerging area of automotive catalysis, so far not mentioned in this article, the treatment of lean-combustion exhaust. Here, the problem is mainly one of removing NO

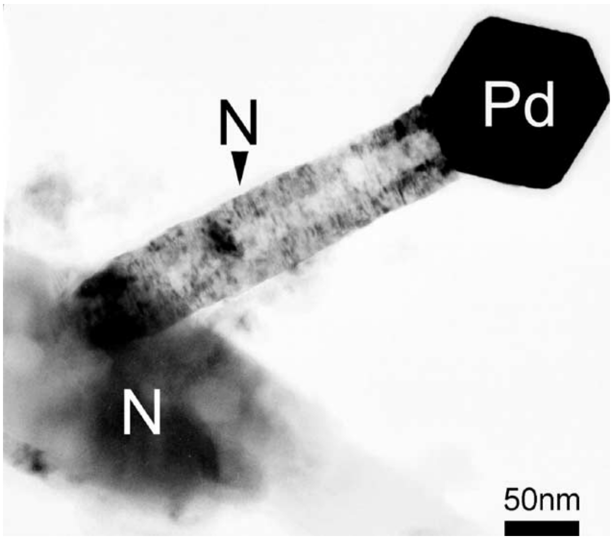

Fig. 10. TEM image of a $Ni_xAl_2O_{3+x}$ ($x \leqslant 1$) nanotube (N) attached to a Pd particle and a larger crystal of $Ni_xAl_2O_{3+x}$ found in a dyno-aged Pd catalyst (reproduced from [47] with permission from Kluwer Academic/Plenum Publishers).

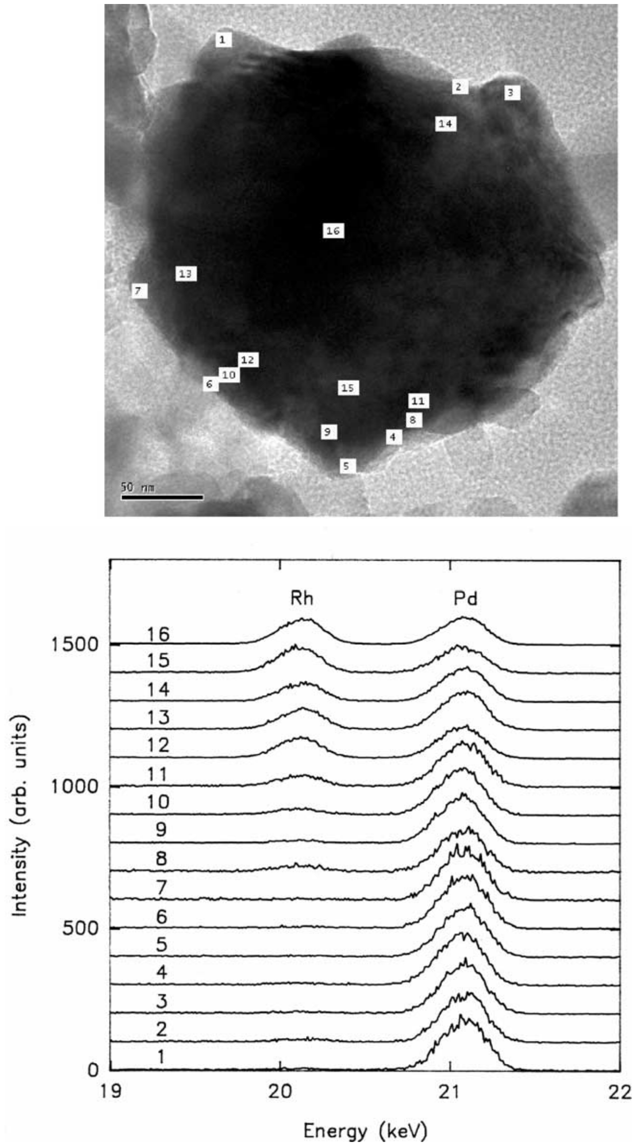

Fig. 11. TEM image and EDS analyses of a large Pd–Rh alloy particle found in a laboratory-aged model bimetallic catalyst following high-temperature aging (reproduced from [48] with permission from Kluwer Academic/Plenum Publishers).

in the presence of oxygen far exceeding the concentration of reductants available. A novel approach, pioneered by Toyota, involves first converting the NO to a solid nitrate which is stored in the "NO_x trap" (under lean conditions), then reducing the stored nitrate to nitrogen under a stoichiometric or rich pulse [49]. More traditional means of NO removal, selective catalytic reduction with or without added reductant, are employed in diesel applications. An additional problem in the case of diesel involves the trapping and combustion of soot particles in a catalyzed filter [50]. While strategies for lean-burn gasoline and diesel have been substantially developed over the past 5–10 years, the underlying technologies are immature compared with that of the TWC, and there currently appears to be the need to use relatively large quantities of Pt. Future research will undoubtedly focus on improved catalysts for low-temperature NO oxidation, needed for both NO_x traps and self-cleaning diesel particulate traps, means to enhance selective catalytic reduction of NO_x, and even the discovery of totally new catalysts for reduction of NO_x under lean conditions.

Acknowledgments

Carolyn Hubbard, Haiping Sun (of the University of Michigan), and Jon Hangas kindly provided Figs. 8, 9, and 10, respectively, prior to their publication.

References

[1] M. Shelef, Catal. Rev. Sci. Eng. 11 (1975) 1.
[2] M. Shelef, K. Otto, N.C. Otto, Adv. in Catal. 27 (1978) 311.
[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, in: Kirk–Othmer Encyclopedia of Chemical Technology, Vol. 9, 4th ed., Wiley–Interscience, New York, 1994, p. 982.
[7] R.M. Heck, R.J. Farrauto, Catalytic Air Pollution Control: Commercial Technology, Van Nostrand Reinhold, New York, 1995.
[8] M. Shelef, R.W. McCabe, Catal. Today 62 (2000) 35.
[9] R.J. Farrauto, R.M. Heck, Catal. Today 51 (1999) 351.
[10] M. Shelef, H.S. Gandhi, Plat. Metals Rev. 18 (1) (1974) 1.
[11] H.S. Gandhi, H.K. Stepien, M. Shelef, Paper No. 750177, Society of Automotive Engineers, 1975.
[12] H.S. Gandhi, H.K. Stepien, M. Shelef, Mater. Res. Bull. 10 (1975) 837.
[13] G.L. Bauerle, J.D. Pinkerton, K. Nobe, Atm. Environ. 8 (1974) 217.
[14] R.J.H. Voorhoeve, J.P. Remeika, L.E. Trimble, Mater. Res. Bull. 9 (1974) 1393.
[15] K.C. Taylor, J.C. Schlatter, J. Catal. 63 (1980) 53.
[16] H.S. Gandhi, W.B. Williamson, E.M. Logothetis, J. Tabock, C. Peters, M.D. Hurley, M. Shelef, Surf. Interface Anal. 6 (4) (1984) 149.
[17] T.J. Truex, Paper No. 1999-01-1543, Society of Automotive Engineers, 1999.
[18] H.S. Gandhi, M. Shelef, Appl. Catal. 77 (1991) 175.
[19] H.C. Yao, S. Japar, M. Shelef, J. Catal. 50 (1977) 407.
[20] H.C. Yao, H.K. Stepien, H.S. Gandhi, J. Catal. 61 (1980) 547.
[21] C. Wong, R.W. McCabe, J. Catal. 119 (1989) 47.
[22] D. Duprez, G. Delahay, H. Abderrahim, J. Grimblot, J. Chim. Phys. 83 (1986) 465.
[23] J.G. Chen, M.L. Colaianni, J.T. Yates Jr., G.B. Fisher, J. Phys. Chem. 94 (1990) 5059.
[24] R.W. McCabe, R.K. Usmen, K. Ober, H.S. Gandhi, J. Catal. 151 (1995) 385.
[25] D.D. Beck, T.W. Capehart, C. Wong, D.N. Belton, J. Catal. 144 (1993) 311.
[26] C.Z. Wan, J.C. Dettling, Stud. Surf. Sci. Catal. 30 (1987) 369.
[27] J.G. Nunan, W.B. Williamson, H.J. Robota, Paper No. 960798, Society of Automotive Engineers, 1996.
[28] G.W. Graham, T. Potter, R.J. Baird, H.S. Gandhi, M. Shelef, J. Vacuum. Sci. Technol. A 4 (3) (1986) 1613.
[29] J.G. Nunan, W.B. Williamson, H.J. Robota, M.G. Henk, Paper No. 950258, Society of Automotive Engineers, 1995.
[30] Y.-K. Lui, J.C. Dettling, Paper No. 930249, Society of Automotive Engineers, 1993.

[31] H. Yao, H. Gandhi, M. Shelef, in: B. Imelik, et al. (Eds.), Metal-Support and Metal-Additive Effects in Catalysis, Elsevier, Amsterdam, 1982, p. 159.

[32] W.B. Williamson, D. Lewis, J. Perry, H.S. Gandhi, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984) 531.

[33] H. Gandhi, H. Yao, H. Stepien, in: A. Bell, L. Hegedus (Eds.), Catalysis Under Transient Conditions, in: Symp. Ser., No. 178, Am. Chem. Society, Washington, DC, 1982, p. 143.

[34] K. Adams, H. Gandhi, Ind. Eng. Chem. Prod. Res. Dev. 22 (1983) 207.

[35] H. Muraki, H. Sinjoh, Y. Fujitani, Appl. Catal. 22 (1986) 325.

[36] H. Muraki, K. Yokota, Y. Fujitani, Appl. Catal. 48 (1989) 93.

[37] H. Muraki, H. Shinjoh, H. Sobukawa, K. Yokota, Y. Fujitani, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 202.

[38] R.W. McCabe, J.M. Kisenyi, Chem. Ind. (7 August 1995) 605.

[39] R.K. Usmen, R.W. McCabe, G.W. Graham, W.H. Weber, C.R. Peters, H.S. Gandhi, Paper No. 922336, Society of Automotive Engineers, 1992.

[40] J.C. Summers, W.B. Williamson, M.G. Henk, Paper No. 880281, Society of Automotive Engineers, 1988; SAE Trans. 97 (1988) 158.

[41] J.C. Summers, J.J. White, W.B. Williamson, Paper No. 890794, Society of Automotive Engineers, 1989; SAE Trans. 98 (1989) 360.

[42] J. Dettling, Z. Hu, Y.K. Lui, R. Smaling, C.Z. Wan, A. Punke, in: A. Frennet, J.-M. Bastin (Eds.), Studies in Surface Science and Catalysis, Vol. 96, Elsevier, Amsterdam, 1995, p. 461.

[43] P. Fornasiero, R. DiMonte, G.R. Rao, J. Kaspar, S. Meriani, A. Trovarelli, M. Graziani, J. Catal. 151 (1995) 168.

[44] T. Murota, T. Hagasawa, S. Aozasa, H. Matsui, M. Motoyama, J. Alloys Compounds 193 (1993) 298.

[45] M. Shelef, G.W. Graham, R.W. McCabe, in: A. Trovarelli (Ed.), Catalysis by Ceria and Related Materials, Imperial College Press, London, 2002, p. 343.

[46] H.P. Sun, G.W. Graham, X.Q. Pan, C.H.F. Peden, S. Thevuthasan, Microscopy and Microanalysis (Microscopy and Microanalysis—2002 Proceedings Supplement), in press.

[47] J. Hangas, Catal. Lett., in press.

[48] G.W. Graham, H. Sun, W.-W. Jen, X.Q. Pan, R.W. McCabe, Catal. Lett. 81 (2002) 1.

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

[50] P. Hawker, N. Myers, G. Hüthwohl, H.T. Vogel, B. Bates, L. Magnusson, P. Bronnenberg, Paper No. 970182, Society of Automotive Engineers, 1997.