

THREE WAY CONVERSION CATALYSTS FOR AUTOMOTIVE POLLUTION ABATEMENT

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INTRODUCTION

The revisions to the Clean Air Act of 1990 and recent regulatory actions taken by the California Air Resources Board mandate the development of automobiles with much lower tailpipe emissions. For the original equipment manufacturers (OEM's) to meet the target fleet emissions numbers for automobiles defined in California's Low Emission Vehicle program, the OEM's must qualify each model into one of the emissions categories defined in Table 1. The emissions are calculated using the Federal Test Procedure (FTP) protocol wherein a test vehicle fitted with a catalytic converter is driven on a chassis rolls over a tightly defined driving cycle. A key feature of the evaluation is that the FTP is conducted after the catalyst has dealt with 50,000 - 100,000 miles of raw engine exhaust. During the FTP, 50 - 80% of the total pollutants emitted to the atmosphere by the vehicle occurs immediately following the startup of the engine when the engine block and manifold are cold, and the catalytic converter has not reached high conversion efficiencies, and are known as "cold start" emissions. The stringency of the regulations becomes evident when to qualify for either Low Emission Vehicle (LEV) or Ultra Low Emission Vehicle (ULEV) status, the hydrocarbon engine out emissions of 2.0 g/mile, typical for a six cylinder vehicle, must be reduced over the entire FTP by 97% and 99%, respectively. These regulations spurred a variety of new technology thrusts aimed at attacking the cold start hydrocarbons including electrically heated catalysts, hydrocarbon traps, exhaust gas burners, and close coupled catalysts (1).

The FTP test poses a unique catalytic challenge. After tens of thousands of startups and shutdowns, the three way conversion (TWC) catalyst must respond excellently, and rapidly to a wide range of operating conditions: Gas hourly space velocities and exhaust gas temperatures can both quickly jump two orders of magnitude in either direction, and the reactant species present in the exhaust gas vary moment-by-moment in composition, concentration, and relative ratio of oxidants to reductants. To meet these stringent emission levels three way conversion catalyst technologies have undergone a fundamental shift in composition and structure to address the needs for lower light-off temperatures, higher thermal durability, and better tolerance to sulfur poisoning. Much of the research effort has been devoted to mediating the primary deactivation mode for TWC catalysts, thermal sintering of both the precious metals and the base metal oxides. This talk will discuss the base metal and precious metal chemistries that have been blended into these durable heterogeneous catalysts for the efficient conversion of auto exhaust gases.

RESULTS AND DISCUSSION

Palladium has a well documented reputation for both hydrocarbon and CO oxidation (2). When our research began on palladium, this metal was known to damage rhodium's NOx efficiencies via the formation a palladium/rhodium alloy and by itself would give only moderate to low NOx conversion efficiencies. Since the functionality of the precious metal is strongly influenced by the surface upon which it sits, rare earth oxides were examined for their NOx promotional effects on palladium. The palladium-only catalysts were formulated utilizing washcoated cordierite (400 cpsi) substrates prepared from slurries containing mixtures of catalyst powders impregnated with palladium nitrate solutions and other oxide additives. All catalysts were aged to simulate in-use catalyst performance in a laboratory honeycomb reactor kept at 1223 K for 12 hr using a simulated auto exhaust gas stream or as full size pieces aged on engine test beds for 75 - 95 hr with a maximum bed temperature of 1193 K. Figures 1(a) and 1(b) summarize laboratory reactor data showing the promotional effects of the rare earth oxides on palladium for NOx reduction and CO oxidation respectively. In the absence of sulfur, the oxides of lanthanum, neodymium, and cerium improved NOx performance, whereas CO performance was only improved by the ceria. Interestingly, only ceria caused both the CO and NOx performances to increase as the temperature was raised. Apparently in the low temperature regime, the catalysis occurs on the palladium, whereas at higher temperatures the catalytic functionality of the ceria is activated and moves the palladium CO/NOx catalysis to a new performance level. However, the benefits of an intimate palladium-ceria interaction for CO/NOx proved a detriment for hydrocarbon activity, especially at elevated temperatures.

With lead levels in the U.S. fuel supply now well below 1 ppm, the most influential fuel component on catalyst performance is sulfur. Sulfur poses a number of challenges to the functioning of TWC catalysts via its interference with both precious metal and base metal function. The sulfur effect on the rare earth oxide promoters for the palladium-only catalysts was examined in the laboratory reactor. Figure 2 demonstrates how lean aging in the presence of sulfur lowered NO_x activity via formation on an intermediate surface oxysulfate on the rare earth oxide. The loss in high temperature ceria performance was particularly notable, but fortunately the oxygen storage function can be restored by subsequent stoichiometric operation.

These findings were then used to create a new palladium-only catalyst architecture wherein the NO_x and HC activities were segregated into separate catalytic layers. For best NO_x performance the topcoat was formulated to contain the oxides of lanthanum, neodymium, and cerium so that their NO_x promoting activity would have first access to the CO for NO_x conversion. The bottom coat was kept ceria-free so as to maintain palladium's hydrocarbon and CO oxidation activity. A 0.69 liter palladium-only honeycomb catalyst, at 3.5 g/l palladium, was aged on an engine test bed using 300 ppm sulfur containing gasoline for 75 hr along with a production 5/1 platinum/rhodium catalyst at 1.41g/l of precious metal. The total FTP hydrocarbon/CO/NO_x conversions efficiencies for the palladium-only catalyst on a 4.6 l vehicle was 95.1%/84.4%/84.1% versus the platinum-rhodium catalyst performance of 89.8%/80.5%/81.9%. The palladium catalyst gave the best hydrocarbon and NO_x efficiencies and proved the catalyst formulation strategy of keeping the NO_x reduction function separate from the hydrocarbon oxidation components..

The palladium-only catalyst showed sensitivity to the sulfur concentration in the exhaust gas in the low temperature regimes. In seeking to maintain the excellent hydrocarbon activity of palladium, but instill better sulfur tolerance into TWC catalysts, we investigated augmenting the best features of the palladium-only catalyst with platinum and rhodium. A Box-Behnken experimental design was employed with the metal loadings of 0 to 0.47 g/l for platinum, 1.41 to 5.65 g/l for palladium, and 0.09 to 0.37 g/l for rhodium. The catalysts were aged in 10% H₂O/90% air at 677 K for four hours. The catalysts were then evaluated on an engine test stand and the results of sweep test evaluations carried out at 673 K under stoichiometric conditions are summarized as contour performance plots for each pollutant in Figure 3. The contour plots show the metals work together synergistically to deal with the pollutants. Palladium makes the greatest contribution to the performance of the trimetal catalysts leading to improved performance for all three pollutants as the palladium content in the catalysts increases. The roles of platinum and rhodium can also be discerned from the contour plots where rhodium contributes to NO_x conversion and the platinum, especially at high palladium levels contributes significantly to CO and NO_x activity. The trimetal formulations also showed an improvement in sulfur tolerance. Experiments were conducted with a production 5/1 platinum/rhodium TWC catalyst at 1.41 g/l of precious metal versus a trimetal catalyst designated ETM II with a precious metal loading of 3.71 g/l with a platinum/palladium/rhodium ratio of 1/14/1. Both catalysts were aged on a fuel cut aging cycle with an inlet temperature of 1173 K. FTP tests were conducted at various fuel content levels on a 2.0 liter vehicle fitted with multiport injectors. The catalyst volumes used in these experiments were approximately one-half what would be used in serial production to accentuate the impact of sulfur on TWC performance. At 300 ppm fuel sulfur, ETM II outperformed the platinum/rhodium catalyst for all three pollutants giving FTP g/mile emissions for hydrocarbons/CO/NO_x of 0.79/3.4/1.05, whereas the platinum/rhodium catalyst gave 0.76/4.5/1.4. Sulfur had little impact on either catalyst for hydrocarbon conversion between sulfur concentrations of 50 - 300 ppm. However, when the sulfur content in the fuel was raised from 50 and 150 ppm both catalysts showed deterioration in CO and NO_x conversion efficiencies. The platinum/rhodium catalyst allowing tailpipe CO and NO_x emissions to increase from 3.4 to 4.4 g/mile and 1.15 to 1.45 g/mile, respectively. ETM II showed the same trends with CO increasing from 3.1 to 3.4 g/mile and NO_x from 0.80 to 1.05 g/mile. Although ETM II proved more resilient to sulfur and the deactivation is reversible by high temperature exposure, continued research is required to develop strategies that mediate sulfur's impact on both the precious metal and oxygen storage components.

SUMMARY

The NO_x performance of palladium-only TWC catalysts were substantially improved by bringing oxides of lanthanum, neodymium, and ceria into intimate contact with the palladium in the topcoat of a two coat catalyst formulation. The concepts used to improve the palladium-only catalyst were successfully applied to trimetal formulations which in turn proved to be more sulfur tolerant than corresponding platinum/rhodium catalyst.

REFERENCES

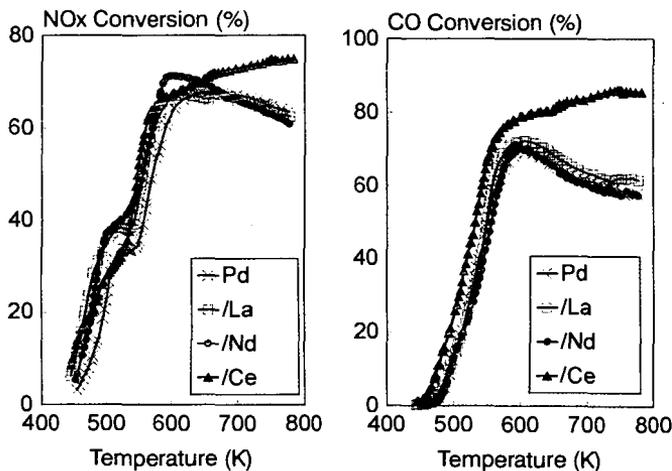
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Table 1.
California's Low Emission Vehicle Program Certification Standards

Low Emission Vehicle Category	Federal Test Procedure (grams/mile) ^{a)}		
	Nonmethane Organic Gases	CO	NOx
Transition	0.125	3.4	0.4
Low	0.075	3.4	0.2
Ultra Low	0.040	1.7	0.2
Zero	0.000	0.0	0.0

^{a)} Emissions after 50,000 miles

Figure 1 (a & b). Laboratory reactor data on aged Pd cores containing 1.75 g/l Pd and 12.2 g/l rare earth oxides



evaluated in a simulated exhaust gas of 0.75% CO, 0.25% H₂, 0.6% O₂, 1600 ppm NO, 280 ppm propene, 16.3% CO₂, 10% H₂O and N₂ balance at 50,000hr⁻¹.

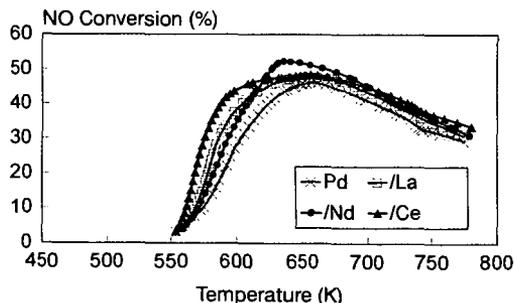


Figure 2. Laboratory reactor data on Pd cores containing 1.75 g/l Pd and 12.2 g/l rare earth oxides after aging in 10%H₂O/90% air and 40 ppm SO₂.

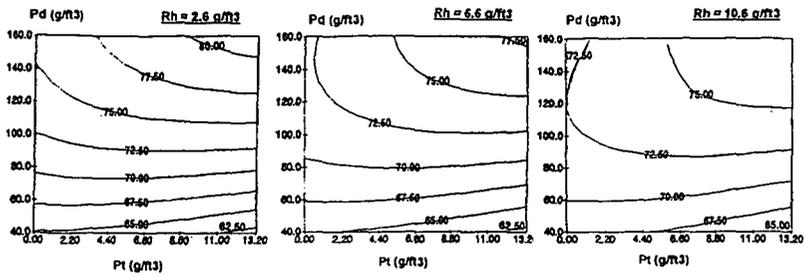


Figure 3(a). Hydrocarbon conversion activities.

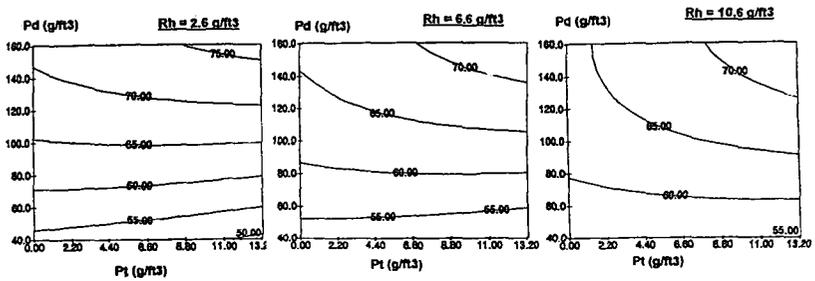


Figure 3(b). CO conversion activities.

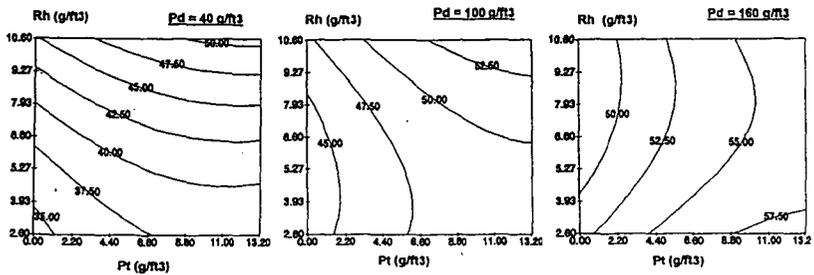


Figure 3(c). NO conversion activities.