

Dynamic Behavior of Automotive Catalysts

III. Transient Enhancement of Water-Gas Shift over Rhodium

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The participation of the water-gas shift reaction in the transient response of Rh-containing catalysts in exhaust was demonstrated by comparing the responses of a Pt/Rh/Ce/Al₂O₃ catalyst, a Rh-free Pt/Ce/Al₂O₃ catalyst, and a Ce-free Pt/Rh/Al₂O₃ catalyst. Each of the bead-type catalysts was mounted in a converter in the exhaust system of a gasoline engine. Infrared diode laser spectroscopy was used to measure CO concentrations in exhaust simultaneously at the converter inlet and outlet with high time-resolution. In the first series of experiments, a catalyst was stabilized under rich exhaust and then given a 1-s exposure to lean exhaust. Following the subsequent lean-to-rich transition, a transient reduction in CO emission was observed over all three catalysts. The reduction in CO emission over the Pt/Ce catalyst could be explained by reaction of CO with oxygen "stored" in the catalyst and CO adsorption and accumulation in the catalyst. The reductions in CO emissions over the two Rh-containing catalysts were greater than the amounts that could be explained by CO and oxygen accumulation and reaction but were consistent with a transient enhancement of the water-gas shift reaction over Rh. Lean-to-rich step response experiments provided further evidence of the participation of water-gas shift in the dynamic behavior of three-way automotive catalysts. During air-fuel ratio cycling and the warmed-up portion of the Federal Test Procedure, time-averaged CO conversions decreased in the order Pt/Rh/Ce > Pt/Ce > Pt/Rh. This ranking suggests that oxygen accumulation and reaction over Ce contributes somewhat more to CO conversion during driving than water-gas shift over Rh. © 1985 Academic Press, Inc.

INTRODUCTION

In 1975, Pt/Pd/Al₂O₃ catalysts were supplied with most new U.S. gasoline-fueled automobiles to control the emission of CO and hydrocarbons. These catalysts operated under lean (net-oxidizing) conditions at all times and essentially complete conversion of CO and hydrocarbons was obtained following catalyst warm-up. In 1981, the need for catalytic control of NO emissions led to the addition of Rh and operation of the catalysts under stoichiometrically balanced conditions after warm-up. Operation in stoichiometric exhaust, while allowing control of NO emissions, also led to decreased conversion of CO and hydrocarbons over these "three-way catalysts."

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In some automobiles a second, oxidation catalyst and injection of supplementary air is required following the three-way catalyst to provide cleanup of CO and hydrocarbons. There are substantial economic incentives to increasing the CO and hydrocarbon conversion performance of three-way catalysts in order to eliminate the need for the air-injection pump and the second catalyst.

Actually, three-way catalysts operate in stoichiometric exhaust only momentarily: the exhaust composition changes rapidly and is stoichiometric only on the average. This is because the step-like response characteristics of the exhaust oxygen sensor and the rapidly changing operating conditions of an automobile lead to rapid oscillation of the air-fuel ratio and the exhaust stoichiometry between rich (net-reducing) and lean (net-oxidizing) conditions. CO and

hydrocarbons are emitted during the rich excursions. In previous reports (1, 2) we have demonstrated that CO conversion following a lean-to-rich transition does not fall instantaneously from the high conversion obtained under lean conditions to the lower conversion expected under rich conditions: transient chemical processes occurring in the catalyst lead to enhanced conversion of CO. Identification and enhancement of these processes should allow improvement of the CO conversion performance of three-way catalysts.

The accumulation or "storage" of oxygen in lean exhaust and the subsequent conversion of CO in rich exhaust by reaction with this stored oxygen has been demonstrated to be an important transient process that affects the dynamic behavior of three-way catalysts (3, 4). A second transient process is the adsorption and accumulation of CO over the precious metals following a lean-to-rich transition and reaction of the adsorbed CO with O₂ and NO during the subsequent rich-to-lean transition (4, 5).

A possible third transient process was identified by Schlatter and Mitchell (6) in laboratory experiments using SO₂-free synthetic exhaust. They found that Rh-containing catalysts became active, temporarily, for the water-gas shift reaction in reducing feedstreams following exposure of the Rh to an oxidizing feedstream. Schlatter and Mitchell proposed that (1) a surface Rh oxide forms under oxidizing conditions that is active for the water-gas shift reaction, and (2) the surface Rh becomes reduced and inactive for this reaction with increasing time of exposure to reducing conditions. However, they found that when SO₂ was added to the feedstreams at a level characteristic of that found in exhaust (ca. 20 ppm SO₂), the period of enhanced conversion following a lean-to-rich step change either disappeared or became too short to be observed with their conventional exhaust analyzers. Thus, the question remained whether this process can occur to a significant extent in

engine exhaust. In this report we demonstrate that it can.

EXPERIMENTAL

Catalysts

The characteristics of the three catalysts are listed in Table 1. The catalysts were prepared by impregnation of alumina beads to incipient wetness with aqueous solutions of H₂PtCl₆, RhCl₃ · 3H₂O, and Ce(NO₃)₃. Following drying, the catalysts were calcined in air at 770 K for 4 h and exposed to engine exhaust for several hours before use in the experiments.

Apparatus

A block diagram of the experimental system is shown in Fig. 1. The 5.7-liter V8 gasoline engine was operated at 1700 rpm with an intake manifold pressure of 54 kPa (abs) on Indolene Clear fuel. The sulfur content of the fuel was such that the exhaust contained approximately 20 ppm SO₂. Exhaust from both manifolds joined at a tee and

TABLE 1
Catalyst Properties

Support: transitional-Al ₂ O ₃			
Bead diameter, cm			0.32
Bead density, g cm ⁻³			0.76
Surface area, m ² g ⁻¹			105
Pore volumes, cm ³ g ⁻¹			
Macro			0.41
Micro			0.57
Pore radii, nm, volume-averaged			
Macro			430
Micro			10
	Metals ^a		
Loadings, μmol g ⁻¹	Pt/Rh/Ce	Pt/Ce	Pt/Rh
Pt	2.6	2.6	2.6
Rh	0.5	0	0.5
Ce	143	143	0

^a The Pt and Rh were located in the outer 25 μm of the beads and the Ce was distributed uniformly throughout the beads.

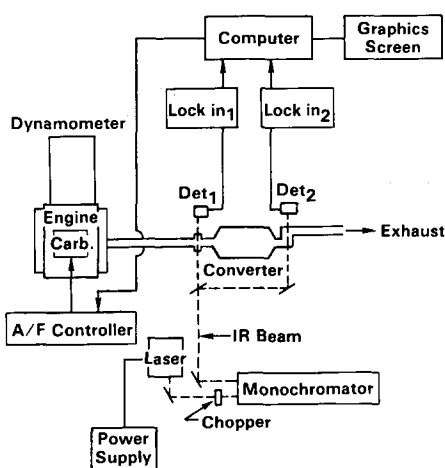


FIG. 1. Schematic of the apparatus.

flowed to the inlet of a standard GM single-bed catalytic converter. The converter was filled with 2620 cm^3 (1370 g) of catalyst beads. The flow rate of exhaust through the converter was $3.6 \times 10^4 \text{ cm}^3 \text{ s}^{-1}$ (including H_2O vapor and corrected to STP) which resulted in a space velocity of $50,000 \text{ h}^{-1}$ (STP). Exhaust temperatures at the converter inlet ranged between 740 and 750 K, depending on the air-fuel ratio (A/F).

Taps before and after the converter (not shown) carried small streams of exhaust to a set of standard exhaust analyzers. These analyzers were used to determine the concentrations of CO, NO, O_2 , CO_2 , and hydrocarbons at the inlet and outlet of the converter. Because of their slow characteristic response times (ca. 1–10 s), the analyzers were used only to determine the time-averaged values of the concentrations under constant engine operating conditions. The average A/F obtained under constant operating conditions was computed using the average concentrations of CO, NO, O_2 , and hydrocarbons, the hydrogen/carbon atom ratio of the fuel (1.91), and the following assumptions: (1) H_2 is present in exhaust at one-third the level of CO, and (2) hydrocarbons can be expressed as propylene equivalents. The stoichiometrically balanced mass A/F, the "stoichiometric point," with this fuel is 14.6.

Table 2 lists the engine-out exhaust compositions obtained at the stoichiometric point and at the rich and lean A/F settings used in this work. All concentrations in this work are given in units of volume percentage of the component in exhaust after removal of H_2O from the exhaust. H_2O is present in exhaust at a level of about 10%.

The lean A/F setting was obtained by adjusting the carburetor. The rich A/F setting was obtained by adding additional fuel through a standard fuel injector which was fitted into a spacer mounted between the carburetor and the intake manifold. The A/F setting was changed in steps or was cycled in square waves by turning the fuel injector on and off with a command from the computer.

CO concentrations in the exhaust flowing into and out of the converter were determined by measuring the absorption of infrared radiation from a semiconductor diode laser turned to the center of the CO P7 absorption line at 2127.685 cm^{-1} . BaF_2 windows mounted on the exhaust pipe allowed one infrared beam to pass through the exhaust flow at the inlet of the converter and the other beam to pass through the exhaust flow at the outlet of the converter. The 10–90% response time of the laser system to a step change is 0.025 s at the output of the lock-in amplifiers. This response time is

TABLE 2
Engine-Out Exhaust Compositions^a

	Air/fuel ratio		
	14.1	14.6	15.1
CO, vol%	1.3	0.6	0.28
HC, ^b vol% (as C_3H_6)	0.062	0.052	0.040
NO, vol%	0.099	0.010	0.10
O_2 , vol%	0.28	0.58	1.1

^a All values are averages and are reported on a dry basis. Both H_2O and CO_2 are present in exhaust at levels of about 10%. H_2 is present in exhaust at about one-third the level of CO.

^b Hydrocarbons.

sufficiently fast to follow accurately all concentration changes which occur in exhaust. Further details are given elsewhere (2, 7, 8).

Measurements of CO emissions during the 1978 EPA driving cycle, commonly called the Federal Test Procedure (FTP), were obtained with the single-bed three-way converter mounted on a 1982 Buick LeSabre with a 4.1-liter V6 engine.

Procedure

All of the laser data shown were obtained by averaging infrared transmitted intensity measurements over a series of experiments performed in immediate succession under computer-control of the A/F setting. The variations in infrared intensity that were averaged were determined to be small enough that correct values of average CO concentrations were obtained. Previously, we determined that steady-state lean conditions were obtained over the catalysts within 20 s and that steady-state rich conditions were obtained within 40 s. The experiments in which the catalyst was stabilized in rich exhaust and then exposed to 1 s of lean exhaust were performed by repeatedly switching the A/F to the rich setting for 40 s, then to the lean setting for 1 s, etc. The lean-to-rich step change experiments were performed by repeatedly switching the A/F to the lean setting for 20 s, then to the rich setting for 40 s, etc. Unaveraged concentration data can be seen in Part II (2).

For each of the experiments, the CO concentration response curve measured at the converter outlet is compared to the CO response curve that would have been obtained if the catalyst were to have responded "instantaneously" to the change in conditions. Our definition of "instantaneous response" and our method of estimating the instantaneous response curves are discussed in detail in Part II (2). Briefly, catalyst response will be instantaneous when two specifications hold: (1) there are no changes in the amounts of reactive species held by the catalyst, and (2) there are no changes in specific activity of the catalyst. When these specifications hold, steady-state conversions will be obtained instantaneously under dynamic conditions. Thus, time-averaged conversion measurements at constant A/F settings were used to estimate the instantaneous response curves, given the measured inlet concentrations and the measured space-time (60 ms) of the plug-flow converter.

RESULTS AND DISCUSSION

Impulse Response

The results of Fig. 2 show the relaxation of CO conversion over each of the three catalysts under which exhaust following a brief (1 s) exposure to lean exhaust. The solid curves are the CO response curves measured at the converter outlet. The dashed curves are the instantaneous re-

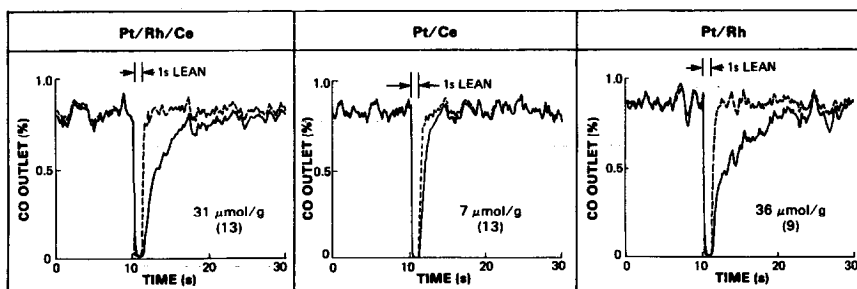


FIG. 2. Impulse response experiments. The A/F setting was switched from 14.1 (rich) to 15.1 (lean) for 1 s, and then back to 14.1. Solid curve: measured CO responses at the outlet of the converter. Dashed curves: instantaneous responses. The curves were obtained by averaging the results of 20 successive experiments.

sponse curves. Purely physical contributions to the response, such as flow around and diffusion within the catalyst pellets, are taken into account in the calculation of the instantaneous response curve. Thus, the discrepancy between the solid and dashed curves is solely a result of transient chemical processes that lead to enhanced conversion of CO.

Our experiments and the way in which the results are presented are very similar to the experiments performed by Schlatter and Mitchell (6) using SO₂-free synthetic exhaust. The difference is that the relaxation of CO conversion occurred over a period of 24 min in the SO₂-free feedstream in (6), rather than over 20 s in exhaust, as seen in Fig. 2.

In each of the plots in Fig. 2, the outlet CO concentration rises to the rich steady-state level more slowly than would be obtained for instantaneous catalyst response. The difference between the solid and dashed curve represents CO that is not emitted from the converter as a result of transient chemical processes occurring within the catalyst beads. The upper number given on each plot is the amount of CO *not* emitted per gram of catalyst. The amounts were determined from the integrated areas between the solid and dashed curves and the flow rate of exhaust.

The noninstantaneous responses of the catalysts indicate that one or both of the two specifications of instantaneous response listed above do not hold: that is, (1) there are changes in the amounts of reactive species held by the catalyst, and/or (2) there are changes in the specific activity of the catalyst.

O₂ is the major oxidant under rich steady-state conditions. Since the conversion of O₂ approaches 100% in rich exhaust, the extra CO that was removed following the lean-to-rich transition must have been removed by adsorption and accumulation of CO over the precious metals and/or reaction of CO with oxidants *other* than gaseous O₂. The possible oxidants are oxygen held by the Ce

compounds, Pt, and Rh in the catalysts (change in accumulation) and H₂O (change in activity).

Schlatter and Mitchell identified the conversion of CO by H₂O over Rh-containing catalysts by (1) measuring the production of CO₂ and H₂ in a rich feedstream composed only of CO, H₂O, and N₂, and (2) showing that instantaneous response was approached in a dry feedstream. Neither of these two options was open to us. The approach we chose was to limit the exposure of the catalysts to lean exhaust in order to limit the extent of enhanced CO removal following the lean-to-rich transition that could be explained by reaction of CO with stored oxygen (plus CO adsorption and accumulation). Observation of significantly greater enhanced CO removal would then demonstrate the participation of the water-gas shift reaction.

The number in parentheses on each plot in Fig. 2 is the maximum amount of CO ($\mu\text{mol CO per g catalyst}$) that could be removed following the lean-to-rich transitions by (1) reaction of CO with oxygen atoms accumulated during the lean exposure (assuming oxidation and reduction between Pt and PtO₂, Rh and Rh₂O₃, and Ce(III) and Ce(IV)), plus (2) adsorption and accumulation of CO over the precious metals (assuming adsorption of one CO molecule per Pt and Rh atom in the catalyst). Since CO conversion approaches 100% during the 1-s lean exposure, we assume that the number of oxygen atoms available for reaction with the catalyst equals the number of oxygen atoms in the 0.5% O₂ and 0.1% NO that remain unconverted in lean exhaust. Over the Pt/Rh/Ce catalyst and the Pt/Ce catalyst, the magnitude of the number in parentheses is limited by the duration of the oxygen exposure, not the capacity for accumulation of reactive oxygen. Over the Pt/Rh catalyst the number in parentheses is limited by the small amount of Pt and Rh in the catalyst, not the short exposure to lean exhaust.

A maximum of 13 $\mu\text{mol g}^{-1}$ of CO could

have been removed by the accumulation/reaction processes over the Pt/Rh/Ce catalyst, whereas $31 \mu\text{mol g}^{-1}$ was actually removed. This discrepancy demonstrates that $18 \mu\text{mol g}^{-1}$ of the enhanced CO removal, or more, was due to the water-gas shift reaction. The response of the Pt/Ce catalyst can be explained by the accumulation/reaction processes alone. This result is in agreement with the experiments of Schlatter and Mitchell: the dramatic effect of the water-gas shift reaction in SO_2 -free feedstreams was limited to Rh-containing catalysts. (However, neither their results nor ours *completely* rule out catalysis of the water-gas shift reaction by Pt and Ce.)

There is an even greater discrepancy between the measured enhanced removal of CO and the amount explainable by accumulation/reaction over the Pt/Rh catalyst than over the Pt/Rh/Ce catalyst, thus providing further evidence for the participation of the water-gas shift reaction.

Note that the minimum probable contribution of the water-gas shift reaction is not quite the same for the two Rh-containing catalysts: the difference between the responses of the Pt/Rh/Ce and Pt/Ce catalysts ($31 - 7 = 24 \mu\text{mol g}^{-1}$) is somewhat lower than the minimum probable contribution of the water-gas shift reaction over the Pt/Rh catalyst ($36 - 9 = 27 \mu\text{mol g}^{-1}$). Thus, these results do not show the significant enhancement by Ce of the water-gas shift reaction over Rh found by Schlatter and Mitchell.

Experiments were conducted in order to determine the duration of exposure to lean exhaust necessary to obtain lean steady-state conditions with respect to CO conversion. Figure 3 shows how the extent of enhanced CO removal over the Pt/Rh/Ce catalyst increased with the duration of exposure to lean exhaust. The maximum enhancement in CO removal was obtained within 5 s of exposure to lean exhaust. This was also the case with the Pt/Ce catalyst. Measurements with lean exposures between 1 and 20 s were not made with the Pt/Rh catalyst, however, 80% of its maximum

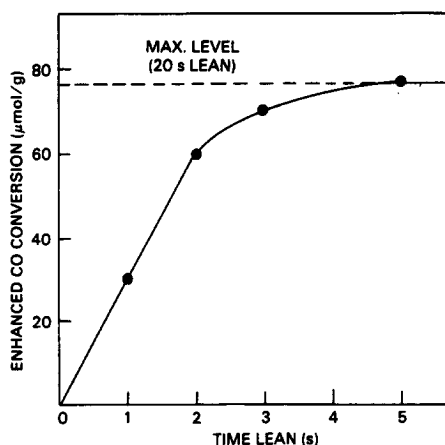


FIG. 3. Increase in enhanced CO conversion over the Pt/Rh/Ce catalyst with increased exposure to lean exhaust. The rich and lean A/F settings were 14.1 and 15.1, respectively.

response was obtained with a 1-s exposure so we expect that the maximum response would be closely approached with a 2-s exposure.

Step Response

Figure 4 presents the responses of the three catalysts following a step change in A/F setting to 14.1 (rich) after stabilization of the catalysts at an A/F setting of 15.1 (lean). The enhanced CO removal over the Pt/Rh catalyst exceeds the maximum possible due to the accumulation/reaction processes by $35 \mu\text{mol g}^{-1}$, providing further evidence for the water-gas shift reaction. The response of the Pt/Ce catalyst now demonstrates the contribution of the "oxygen storage capacity" of Ce: the enhanced CO removal is 85% of the maximum possible due to the accumulation/reaction processes. The result that it is less than 100% does not rule out some participation by the water-gas shift reaction, of course.

The response of the Pt/Rh/Ce catalyst falls within the limit explainable by the accumulation/reaction processes. However, the earlier results with the 1-s exposure and the fact that the enhanced CO removal is greater than that over the Pt/Ce catalyst makes it probable that the water-gas shift

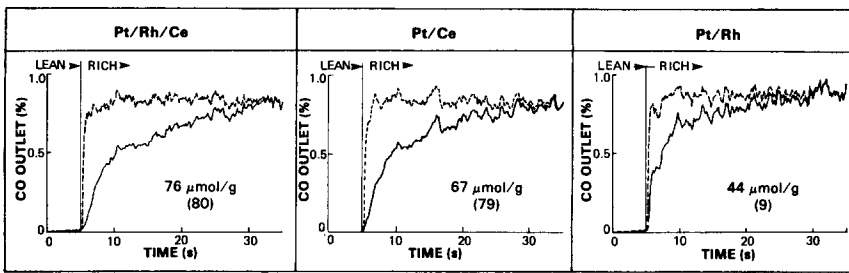


FIG. 4. Step response experiments. The A/F setting was switched from 15.1 (lean) to 14.1 (rich). Solid curves: measured CO responses. Dashed curves: instantaneous responses. The curves were obtained by averaging the results of 20 successive experiments.

reaction is contributing to the step response shown.

The enhanced conversion over the Pt/Rh/Ce catalyst ($76 \mu\text{mol g}^{-1}$) is not equal to the sum of the enhanced conversion over the Pt/Ce catalyst ($67 \mu\text{mol g}^{-1}$) and the estimated contribution of water-gas shift over the Pt/Rh/Ce catalyst in the impulse response experiments ($31 - 7 = 24 \mu\text{mol g}^{-1}$). This discrepancy suggests the presence of complex interactions between Pt, Rh, and Ce which lead to nonadditive effects.

The impulse response experiments show that the enhanced CO conversion by water-

gas shift is activated rapidly. The enhanced conversion by oxygen storage over Ce is activated slowly but, as the step response experiments show, has a greater "capacity" for converting CO.

Frequency Response

Figure 5 shows the response of the catalysts during A/F cycling. The A/F setting was switched in a square wave between 14.1 and 15.1. Equal periods of time were spent at each setting such that the time-averaged A/F was stoichiometrically balanced at 14.6.

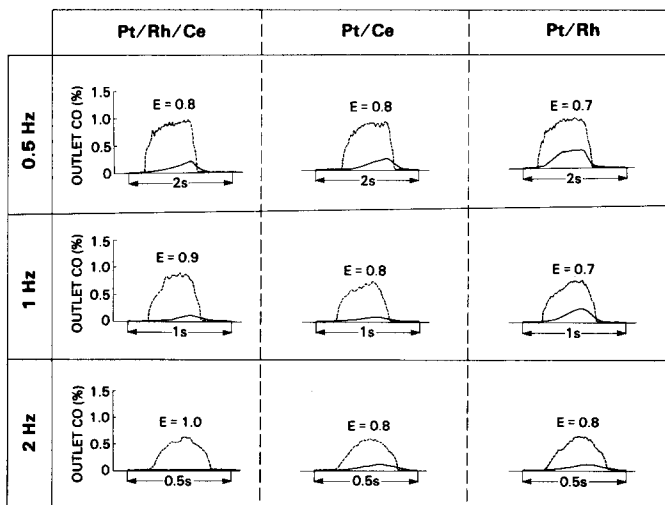


FIG. 5. Frequency response experiments. The A/F setting was switched in a square wave between 14.1 (rich) and 15.1 (lean). Equal periods of time were spent at each setting and the time-averaged A/F (14.6) was stoichiometrically balanced. Solid curves: measured CO responses. Dashed curves: instantaneous responses. The curves were obtained by averaging the results of 30 successive cycles. The conversion enhancement, E , is defined in the text.

Typical inlet CO concentration curves were shown for various cycling frequencies in Part II (2). Mixing processes in the intake manifold of the engine result in attenuation of the amplitude of the exhaust composition oscillations seen by the catalyst (mixing processes in the exhaust manifold and pipe leading to the converter have much smaller effects) (8, 9). This attenuation is reflected by the decreased amplitude of the dashed, instantaneous response curves in the figure at the higher cycling frequencies. Thus, the attenuation of the A/F cycles at the inlet of the converter leads to a decrease in CO emissions from the converter. The noninstantaneous dynamic responses of the catalysts lead to further reductions in CO emissions as the cycling frequency increases, as indicated by the increased discrepancies between the dashed and solid curves at the higher frequencies.

A quantitative measure of the difference between the actual and instantaneous responses for each cycle in the figure is given by E , the "conversion enhancement." For each cycle, E is defined as the area between the dashed and solid curves divided by the total area under the dashed curve. In words, E is the *fraction not emitted* of the CO that would have been emitted if the catalyst's response were instantaneous. Thus, high values of E are desirable. A further discussion of E is presented in Part 2 (2).

Table 3 lists the average CO conversions corresponding to the plots in Fig. 5. During A/F cycling the ranking of the catalysts in order of decreasing performance (increasing CO emission) is Pt/Rh/Ce > Pt/Ce > Pt/Rh. This is the same ranking that was obtained for the step response experiments but differs from the ranking obtained in the impulse response experiments. The agreement between the ranking during cycling and lean-to-rich step changes suggests that the Ce in the Pt/Rh/Ce and Pt/Ce catalysts is more oxidized than reduced during cycling and, thus, can contribute to conversion of CO during the rich periods of the

TABLE 3
Comparison of Average CO Conversions

Cycling between A/F 14.1–15.1 (Hz)	%		
	Pt/Rh/Ce	Pt/Ce	Pt/Rh
0.5	93	92	81
1.0	94	93	85
2.0	97	95	92
Warmed-up portion of FTP (cycles 4–23)	80	71	54

A/F cycles. This suggestion is reasonable since we have shown in this report and in Part I that lean steady-state conditions are attained much faster than rich steady-state conditions following a step change from the opposite A/F setting.

Because the average A/F is stoichiometrically balanced, there is sufficient O₂ and NO in the lean half-cycles to account for the enhanced conversion of CO during the rich half-cycles over each catalyst. In addition, the maximum possible contribution of accumulation/reaction processes over the catalyst with the smallest capacity (9 μmol g⁻¹ over Pt/Rh) is sufficient to account for the largest conversion enhancement observed over this catalyst during cycling (7 μmol g⁻¹ per cycle at 0.5 Hz). However, we feel that it is highly likely, in light of the impulse and step response experiments, that the water-gas shift reaction does contribute to enhanced CO conversion during A/F cycling over the two Rh-containing catalysts.

We have no direct way of determining the relative contributions of the accumulation/reaction processes and the water-gas shift reaction during the cycling experiments. Simultaneous measurements of CO, CO₂, H₂, hydrocarbons, O₂, and NO would be required to make this determination.

FTP Performance

Table 3 also lists the average CO conversions obtained over the catalysts during the warmed-up portion of the Federal Test Pro-

cedure (acceleration-deceleration cycles 4 through 23). For each test, the average conversion was computed from the total amount of CO measured at the converter inlet and the total amount of CO measured at the converter outlet. The numbers listed were obtained by averaging the average conversions obtained from four tests for each catalyst. The CO-conversion performance ranking of the catalysts for the FTP is the same as that for the step and frequency response experiments: Pt/Rh/Ce > Pt/Ce > Pt/Rh. This ranking suggests that oxygen accumulation and reaction over Ce contributes somewhat more to CO conversion during driving than water-gas shift over Rh.

Although conversion measurements during A/F cycling at 1 Hz is frequently used as an indicator of the warmed-up FTP performance of a three-way catalyst, we feel that the step response performance may be more relevant: a detailed analysis of the FTP result shows that CO emissions primarily occur during the relatively large-amplitude, long-duration rich excursions associated with accelerations. Emission of CO during A/F cycling is less important because exhaust flow rates are moderate and conversions are high (note that the average conversions obtained during cycling are significantly higher than the average conversions obtained during the warmed-up portion of the FTP). An analysis of catalyst performance during the warmed-up portion of the FTP will be presented in Part IV.

CONCLUSION

We have shown that the water-gas shift

reaction must be considered when analyzing the CO-conversion performance of three-way automotive catalysts under dynamic conditions in engine exhaust. In addition to time-resolved measurement of CO, time-resolved measurements of other exhaust components (especially O₂) will be necessary in order to determine the relative contributions of the water-gas shift reaction and the accumulation and reaction of CO and oxygen.

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