JOURNAL OF CATALYSIS 56, 321–335 (1979)

Poison-Resistant Catalysts for the Simultaneous Control of Hydrocarbon, Carbon Monoxide, and Nitrogen Oxide Emissions[1]

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Received June 6, 1978; accepted October 4, 1978

The paper investigates several features of the operation of noble metal catalysts in automobile exhaust near the stoichiometric air:fuel ratio (A/F). These features include the extent of intrapellet diffusion limitations as a function of feedstream stoichiometry, the mechanism of poisoning, the effects of noble metal (Pt, Rh, Pd) impregnation profiles on activity and poison resistance, and the effects of A/F oscillations on catalyst performance. A pellet configuration, containing an external shell of Pt and internal rings of Rh and Pd, was found to have improved poison resistance and lightoff characteristics. The addition of Ce improved the catalyst's initial performance in transient operation.

INTRODUCTION

Emission standards legislated for the coming years necessitate a further reduction in hydrocarbons (HC), carbon monoxide, and nitrogen oxides (NO) in the exhaust of automobiles. Catalytic emission control near exhaust stoichiometry, with the application of an oxygen sensor and a closed-loop electronic circuitry, appears to be a promising method to accomplish the above task (*1*).

The performance of different catalytic metals around stoichiometry is related to their ability to reduce NO and oxidize HC and CO in an air:fuel ratio (A/F) window of some practical width around the stoichiometric point. Pt and Pd, noble metals which are currently employed in oxidative emission control, are inadequate to effectively control NO emissions. For this reason, Rh is added to the catalyst: Rh was found to catalyze NO reduction in the presence of traces of O_2 in the feedstream (*2*, *3*).

Although a large number of catalytic metals and metal combinations have been explored in the meantime [for recent reviews, see (*4*), (*5*), and (*6*)], no suitable substitute for Rh has been found to date. Most of the current interest is centered, therefore, around the application of Pt–Rh and Pt–Rh–Pd catalysts for the simultaneous control of HC, CO, and NO emissions.

Rh appears in the Pt ore in a small quantity, so that about 18 parts of Pt have to be mined for 1 part of Rh. If significantly higher quantities were to be used, the extra Rh demand would necessitate a large increase in Rh (and Pt and Pd) mining, with its associated practical and economic implications (*7*). Consequently, there is a strong motivation to develop

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[1] Presented at the 176th National Meeting of the American Chemical Society, Miami Beach, Florida, September 1978.

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0021-9517/79/030321-15$02.00/0

TABLE 1

Properties of the Catalysts Employed

Designation	A	B	C	D	E	F	G
Configuration	Pt-Rh	Pt/Rh	Pt/Rh	Pt/Rh	Pt/Rh//Ce	Pt/Rh/Pd	Pt/Ph/Pd//Ce
Support	A	A	A	B	B	B	B
Pt							
wt%	0.045	0.046	0.041	0.043	0.045	0.048	0.055
Begins (μm)	0	0	0	0	0	0	0
Ends (μm)	100+	106 ± 24	80 ± 30	67 ± 24	57 ± 15	51 ± 8	50 ± 19
Rh							
wt%	~0.0020	0.0025	~0.0020	0.0026	0.0025	0.0026	0.0031
Maximum (μm)	0	68	110	~60	~60	58	60
Ends (μm)	32	200	400	~160	(~160)	132	160
Pd							
wt%	0	0	0	0	0	0.015	0.020
Begins (μm)						121 ± 14	81 ± 18
Ends (μm)						352 ± 60	169 ± 30
Ce							
wt%	0	0	0	0	1.0	0	1.0
Deployment sequence	Coimpregnated	Rh, Pt	Pt, Rh	Rh, Pt	Ce, Rh, Pt	Pd, Rh, Pt	Ce, Pd, Ph, Pt

catalysts which perform adequately at low levels of Rh.

The simultaneous control of HC, CO, and NO emissions in automobile exhaust presents a considerable challenge since much remains unknown about the mechanism and kinetics of the reactions involved—information which would be very useful for the rational design of catalysts. Perhaps for this reason, much of the catalyst development work in this area has been of an empirical nature.

Instead of mounting an empirical search scheme, we decided first to carry out a sequence of experiments which were designed to answer certain questions about the mechanism of operation and mode of deactivation of stoichiometric catalysts, hoping that the results will be useful in designing an improved low-Rh catalyst. In this paper we will discuss certain important aspects of stoichiometric catalyst operation, and combine them into a novel catalyst design. Steady-state and cycled laboratory, engine dynamometer, and vehicle tests will be employed to compare the performance of different catalyst preparations.

EXPERIMENTAL

a. Catalysts

Seven catalyst formulations (Table 1), prepared over two supports (Table 2) will be discussed in detail. Three additional

TABLE 2

Properties of the Catalyst Supports Employed

Designation		A	B
V_{total} (cm^3/g)		0.683	0.887
V_{macro} (cm^3/g)	(pore volumes)	—	0.230
V_{micro} (cm^3/g)		—	0.657
$\bar{r}^a$ (Å)		551	—
$\bar{r}^a_{macro}$ (Å)	(pore radii)	—	18553
$\bar{r}^a_{micro}$ (Å)		—	162
s (m^2/g)	(surface area)	112	129
ρ_p (g/cm^3)	(pellet density)	1.037	0.853
$D^b_{N_2,He}$ (cm^2/sec)	(diffusivity)	0.0126	0.0179
$R_{nominal}$ (cm)	(pellet radius)	0.159	0.159

[a] Integral averaged.

[b] Transient pulse technique, 40°C, 1 atm.

catalysts (containing only Rh) were prepared to explore diffusion effects.

The supports were designed to have low density, high diffusivity, and high surface area, resulting in favorable poison resistance (*8*, *9*). The preparation of multilayered catalysts has been discussed recently (*10*); as we will demonstrate later on, the impregnation of the different metal components in different bands in the catalyst pellets allows one an interesting design flexibility.

All catalysts in Table 1 contain noble metals near the "natural" loading at their current Pt usage level. Catalyst A has been coimpregnated by Pt and Rh in an approximately 100-μm-deep band at the surface of the pellets, while catalysts B to G contain the metals in different bands, as indicated. A, B, and C were prepared by the incipient wetness technique, and D to G were prepared by spraying. In principle, these techniques differ only in the amount of impregnating solution used with respect to the pore volume of the support.

Pt, Pd, and Rh were deposited from their chlorine complexes in an aqueous solution, while Ce was deposited from an aqueous nitrate solution. The subsurface bands were achieved by using either HF (catalysts B and C) or citric acid (catalysts D to G) as site-blocking agents. Such techniques have been described, e.g., in Ref. (*11*). The deployment sequence of the individual noble metal bands is indicated in Table 1.

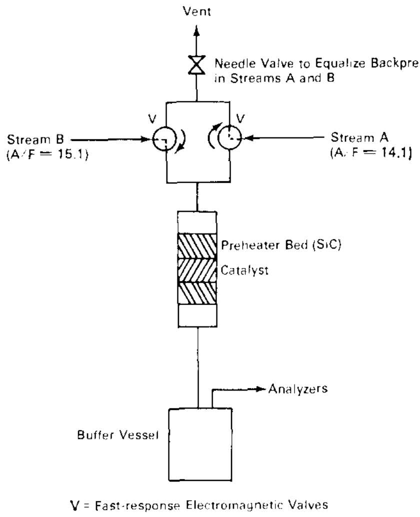

FIG. 1. Laboratory reactor system to study catalysts at oscillating A/F (schematics).

TABLE 3

Feedstreams for the Oscillated Laboratory Experiments[a]

	Stream A[b]	Stream B[b]
A/F (simulated)[c]	14.08	15.12
Propylene (ppm vol)	536	400
NO (ppm vol)	150	250
CO (vol%)	1.09	0.39
CO_2 (vol%)	10.0	10.0
H_2 (vol%)	0.33	0.07
O_2 (vol%)	0.20	1.00
H_2O (vol%)	10.0	10.0
N_2 (vol%)	Balance to 100%	Balance to 100%

[a] See Fig. 1 for explanation.
[b] The mixture of stream A and B gives A/F = 14.59.
[c] Computed from the composition of the feedstream.

After the impregnation of each layer, the catalysts were dried and subsequently fired in air at 550°C for 4 to 5 hr.

Pt and Pd profiles were determined by a staining technique (*11*), while Rh profiles were measured by ion microprobe mass analysis (IMMA), a technique which is especially well suited to detect very low Rh concentrations. Poison (Pb, P) profiles in the catalyst pellets were determined by electron microprobe. The elemental analyses were carried out by X-ray fluorescence and by wet chemical analysis.

The catalyst supports were characterized by ultrahigh pressure Hg porosimetry, N_2 BET, and by a transient N_2–He pulse diffusivity technique (*12*).

b. Laboratory Bench Test with Cycled A/F[3]

A laboratory reactor system has been developed which allows the observation of catalyst performance as a function of A/F oscillation amplitude and frequency,

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[3] For the fuels employed, the stoichiometric A/F is 14.65. A/F < 14.65 is a net reducing exhaust, and A/F > 14.65 is net oxidizing.

TABLE 4

Poison Content of the Test Fuels Employed

	Fuel a	Fuel b	Certification fuel[a]
Pb (g/liter)	0.029	0.012	0.00045
P (g/liter)	0.007	0.014	0.00005[b]
S (g/liter)	0.117	0.117	0.080 (approx.)

[a] Average composition.

[b] In real-time engine operation, much of the P content of the exhaust is due to the engine lubricating oil which contains P components as additives.

at a selected space velocity and operating temperature.

Figure 1 is a schematic representation of the apparatus. Streams A and B represent the two extremes of A/F composition amplitudes. Valves V were simultaneously switched back and forth at a selectable frequency (in the range of <1 to >6 Hz), exposing the catalyst bed to rich and lean mixtures in an alternating fashion. The exhaust of the reactor was mixed in a buffer vessel of 2000 cm^3 volume. This buffer vessel fed the analyzers (for HC, CO, CO_2, NO, NH_3, H_2, and O_2) which then determined the time averaged reactor output level at any selected A/F oscillation frequency. The feedstreams for the experiments discussed in this report are shown in Table 3.

c. *Static Dynamometer Testing and Aging of Stoichiometric Catalysts*

A Chevrolet V-8 engine (5.7 liter volume) was used in this experiment at 1800 rpm, 47 kPa manifold vacuum, no exhaust gas recirculation (EGR), and exhaust flow rate of about 100,000 cm^3/sec (560°C, 1 atm). For activity testing, the A/F was set to selected values, the system was stabilized, and the CO, NO, and HC conversions were determined. The converter inlet and outlet O_2 concentrations were also measured.

For the aging process, the A/F was continuously changed from 13.7 to 15 (in 20 sec) and back (in 20 sec), by moving the choke plate with an electric motor.

A 1000-cm^3 converter was employed which operated at a high space velocity (approximately 130,000 hr^{-1} at 22°C and 1 atm). This had the advantage of suppressing the conversions (from near 100% at low space velocities) to a well-measurable range, so that differences between catalysts became more pronounced and easier to observe.

The inlet temperature to the converter was between about 560 and 570°C. The exit temperatures varied between about 580 and 630°C, depending upon the degree of conversion over the catalyst which determined the amount of heat generated. The compositions of the fuels employed are shown in Table 4. Fuels a and b contained higher P and Pb levels than typical certification fuels. In an earlier publication (*8*) we explained how the time scale of catalyst poisoning experiments is related to the level of poisons in the feedstream to the catalyst. Fuel a was found to approximate 80,000 km poison exposure in about 40 hr, and fuel b in 20 hr.

d. *Dynamometer Tests With Cycled A/F*

All these tests were carried out by the AC Spark Plug Division of General Motors. A 5.7-liter V-8 engine was employed which was operated at 1400 rpm. The A/F oscillated ±0.5 units around its midpoint, with a frequency of 1 Hz. The midpoint was slowly moved from lean to rich, covering an A/F band of about ±0.3 around stoichiometry. The system employed a closed-loop control scheme with an oxygen sensor and an electronic controller. The A/F was modulated by fuel injection below a carburetor which was set to a constant (lean) A/F. Typical output information included CO, NO, and HC conversions (time averaged) and oxygen sensor setpoint, as a function of A/F (calculated from exhaust gas composition).

The converter inlet gas temperature was about 480°C. All the results discussed here were generated on converters with 4261 cm^3 volume. The exhaust gas flow rate was about 33,000 cm^3/sec (20°C, 1 atm) with a corresponding space velocity of 27,900 hr^{-1}. Certification fuel (Table 4) was employed.

e. *Vehicle Tests*

These tests, too, were carried out by the AC Spark Plug Division of General Motors. The car employed a vacuum-modulated carburetor and an oxygen sensor. Typical engine-out emissions during the 1975 FTP[4] were: 2.2 g/mile HC, 11.0 g/mile CO, 2.3 g/mile NO. These car tests involved a cold start, while the above discussed cycled dynamometer tests did not. Consequently, the FTP tests were influenced by the lightoff performance of the catalyst, and this provided a more realistic (and also more complex) measure of catalyst performance. The results discussed here were generated on 4261-cm^3 converters. Certification fuel (Table 4) was employed. The closed-loop emission control system was recently described in Ref. (*1*). Notable is the cyclic nature of A/F control: This is why the cycled bench test and dynamometer test were developed (sections b and d above).

SOME MECHANISTIC ASPECTS OF STOICHIOMETRIC CATALYST OPERATION

In order to attempt a rational catalyst design, we were interested in the differences among Pt, Pd, and Rh, in their interferences with each other when impregnated over the same support, in the extent of diffusion control at various exhaust stoichiometries, and in the mechanism of catalyst poisoning near stoichiometry. We will first briefly discuss these aspects, and then we will show how they were synthesized to arrive at a novel catalyst design.

a. *Differences among the Catalytic Properties of Pt, Rh, and Pd*

Pt, Pd, and Rh are the noble metals which are considered in our catalyst design studies.

Pt and Pd are excellent oxidizing catalysts but they are poor NO reducing catalysts in rich automobile exhaust. Although both Pt and Pd are capable of reducing NO and oxidizing CO near stoichiometry, these metals work only in a narrow A/F window around stoichiometry if both processes are to be catalyzed simultaneously (*13*).

Rh is an excellent NO reducing catalyst, even in the presence of small quantities of O_2 (*2, 3, 14*). However, highly oxidized Rh is a poor oxidizing catalyst (*15*). Because of this, and because of the very small quantities of Rh available, the oxidizing functions of the catalyst have to be supplemented by the addition of Pt and Pd (e.g., *16*).

Pt is more resistant to poisoning than Pd, apparently due to an as of yet unexplained residual activity of the poisoned Pt catalyst (*17*). However, Pd is more resistant to sintering than Pt (*18*), and thus, when the Pd is protected from poisoning in Pt/Pd-oxidizing catalysts (by subsurface impregnation such that the poisons cannot reach it), it provides for an improved lightoff performance in aged catalysts (*10*).

Much less is known about the poison resistance of Rh in automobile exhaust. However, as we will show, if Rh is exposed to a P- and Pb-containing exhaust, it rapidly loses its activity. Due to the very small amounts of Rh, this fact becomes of crucial importance in catalyst design.

b. *Interferences between Pt and Pd, and between Pt and Rh*

In previous studies on Pt-Pd catalysts it was found that when Pt and Pd are coimpregnated over the same catalyst support, the catalyst poisons almost as

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[4] Federal Test Procedure: a prescribed vehicle speed–time schedule for emission testing.

fast as a Pd catalyst (*10*). There are strong implications that a Pt-Pd alloy forms with Pd on the surface. When Pt and Pd were impregnated into separate layers, a marked improvement in catalyst performance resulted (*10*) since the advantages of both of these metals could be gainfully utilized.

Recent reports (*15*) suggest to us that Pt may also alloy with Rh, with Rh at the outer surface. Rh shows a rather peculiar dual-state behavior, depending on its oxidation state (*15*). This manifests itself in highly oxidized Rh having a rather poor oxidizing and reducing ability. Since near stoichiometry the environment may vary from reducing to oxidizing and vice versa, the above interference between Pt and Rh appears to be detrimental to three-way catalyst performance, and thus one would expect an improvement if Rh and Pt were impregnated separately (*15*, *16*).

c. *Extent of Diffusion Control as a Function of Stoichiometry*

Oxidizing catalysts at typical converter temperatures operate near their diffusion limit: The rates of the oxidizing reactions are so fast that the reactants cannot diffuse fast enough to the active sites. This results in sharp reactant (and product) concentration profiles in the porous catalyst pellets, such that only a small fraction of the pellet is supporting the reaction. Due to this excess catalytic activity over the transport limit, the performance of oxidizing catalysts is not very sensitive to the amount of catalytic metals employed, or to loss of catalytic surface (e.g., upon thermal sintering) (*19*). Their sensitivity to poisoning is related to the thickness and diffusive resistance of the poisoned zone which surrounds the still active portions of the catalysts pellets (*8*).

Stoichiometric catalysts operate in an A/F range which covers both oxidizing and reducing environments, and we undertook some simple experiments to explore the degree of diffusion control as a function of feedstream stoichiometry.

Three catalysts were prepared on an alumina support which is similar in its characteristics to support B in Table 2. The catalysts contained approximately 0.002 wt% Rh. Approximately 100-μm-thick Rh bands were deposited either at the outer surface of the pellets, 40 μm below the outer surface of the pellets, or 120 μm below the outer surface of the pellets. This resulted in an inert alumina ring surrounding the active zone, where the depth of this inert zone was varied from 0 to 120 μm.

The conversion of NO, CO, and HC was observed as a function of exhaust stoichiometry, using the static engine dynamometer system and 1000-cm^3 reactor described in section c of the experimental part of this paper. Indolene clear fuel was used.

The results are shown in Fig. 2. The NO reduction reactions are fastest at rich stoichiometries, where the catalysts reach their respective diffusion limits. As the stoichiometry becomes net oxidizing, the intrapellet diffusion effects are minimized, due to the slower rates of the NO reduction reactions. A partial diffusion limitation exists at the stoichiometric point.

The CO oxidation reactions show an opposite trend with A/F: The rates are highest under net oxidizing conditions, where almost complete diffusion control prevails. The effects of diffusion influences diminish as the feedstream becomes net reducing. Again, partial diffusion control prevails at the stoichiometric point.

The HC conversion reactions show a pronounced diffusion effect throughout the A/F range of the experiments. On the oxidizing side, HC conversions are large due to the reaction of HC with O_2, while still appreciable HC conversions occur on the rich side, apparently due to the reaction of HC with H_2O (steam reforming), and with the small amounts of O_2 present (*20*).

The significance of the above observa-

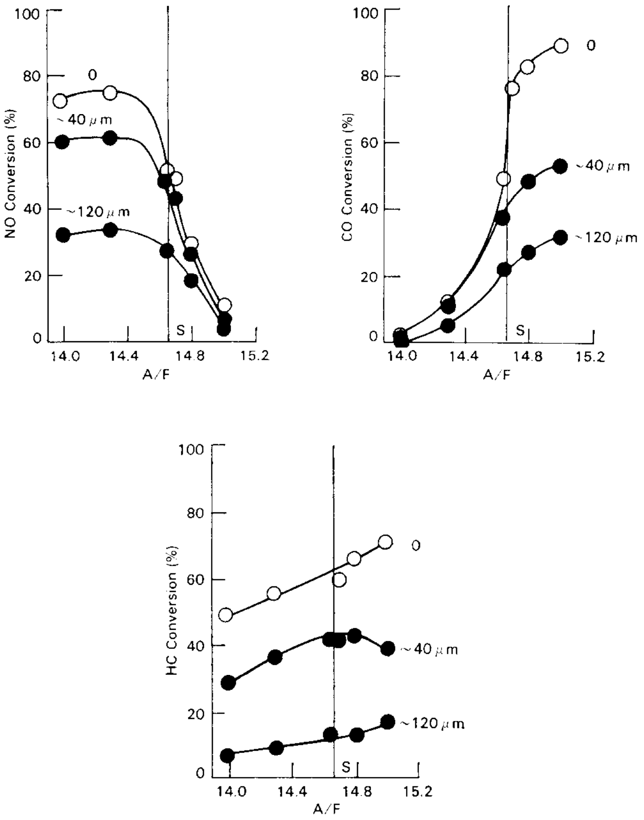

FIG. 2. Effects of Rh location in the catalyst pellets on conversion, as a function of exhaust stoichiometry (static engine dynamometer experiments).

tions can be summarized rather simply: While subsurface impregnation appears to impose a severe diffusion barrier on catalysts operated primarily in the net oxidizing regime or in the net reducing regime, it may be possible to design a stoichiometric catalyst in which the minute quantities of Rh are impregnated somewhat below the surface and thus protected from the poisons (Pb, P) in the feedstream.

d. Poison Deposition as a Function of A/F

In oxidizing catalysis, the poisons tend to penetrate the catalyst pellets in the form of a sharply defined shell, indicative of a diffusion-controlled poison-collecting process (*8*, *21*). Improved oxidizing catalysts were designed by impregnating the pellets in such a way that the poison front could not reach the end of the noble metal impregnated zone during the intended lifetime of the catalyst (*8*). We undertook a series of experiments to determine if the same poisoning mechanism prevails during stoichiometric operation.

A Pt–Rh/alumina catalyst (0.035 wt% Pt, 0.0023 wt% Rh) was exposed to automobile exhaust in our dynamometer. Fuel b in Table 4 was employed. The conditions of the engine dynamometer operation were discussed in the experimental part (section c). After 20 hr of exposure to the poisons, samples were withdrawn from the 1000-cm^3 reactor and analyzed by electron microprobe for poison penetration and by wet chemical analysis for poison collection. The experiment was repeated with the same

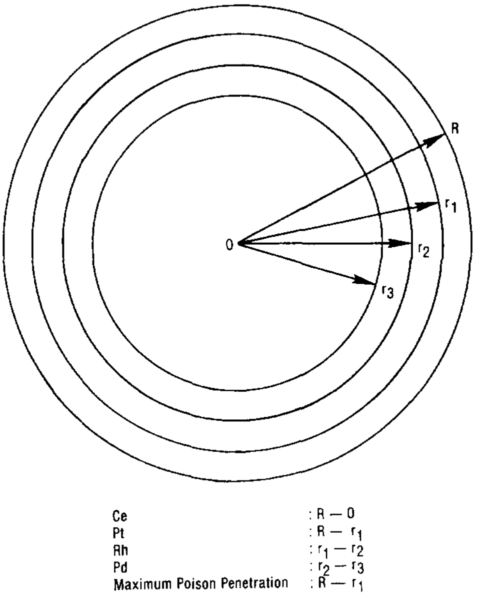

FIG. 3. Low-Rh catalyst design concept.

catalyst at three conditions: net rich (A/F $\simeq$ 14), net lean (A/F = 15), and stoichiometric (A/F = 14.65 ± 0.5, cycled in 20-sec intervals). The integral averaged poison penetrations and poison accumulations indicated that the amount of lead and phosphorus penetrations was only slightly dependent on the stoichiometry employed. The leading edge of the poison front is provided by phosphorus (*10*).

From this we concluded that the poisoning process at exhaust stoichiometry appears to be very similar to the poisoning process under net oxidizing conditions; that is, only a sharply defined outer shell of the pellets is poisoned, this shell progressing inward as time elapses.

DESIGN OF A STOICHIOMETRIC CATALYST WITH IMPROVED PROPERTIES

Based on the mechanistic aspects discussed in parts a to d of the previous section, the following catalyst design concept was developed:

(i) To utilize the different properties of Pt, Pd, and Rh, all three will have to be employed in a successful design. The quantity of these metals for automobile catalysis was fixed at 1.12 g Pt/car (0.036 toz Pt/car), 0.44 g Pd/car (0.014 toz Pd/car), and 0.06 g Rh/car (0.002 toz Rh/car), corresponding to their mine ratio.

(ii) To avoid the interferences of these metals, they should not be coimpregnated over the same support surface. One way to avoid coimpregnation is to impregnate them in separate layers in the catalyst pellets.

(iii) Due to its relative poison insensitivity, Pt should be the outer layer, while Pd and Rh should be protected from the poison front. Consequently, the Pt impregnation depth (from the outer surface to this depth) is given by the depth to which the poisons penetrate. This depth can be easily determined (*8*).

(iv) Due to the importance of Rh in catalyzing the NO reduction reaction at the (diffusion-controlled) rich end of the A/F scale, Rh should be impregnated as close to the surface of the pellet as possible, while still protecting it from poisoning. Consequently, Rh should be impregnated right below the Pt layer, and Pd underneath the Rh layer.

(v) Since less than complete diffusion control prevails near stoichiometry, all three metals are expected to provide useful functions there. In addition, the added Pd should be beneficial during catalyst warmup where kinetic control prevails, at least for the beginning of the process.

(vi) Due to the transient nature of the feedstream's A/F (*1*), it appears to be beneficial to include an agent in catalyst formulations which, by storing and slowly releasing some of the components from the surface, tends to smooth out the effects of A/F oscillations. We chose Ce for this purpose: As we will see, it tends to improve catalyst performance in a cycled feedstream.

The above catalyst design concept is summarized in Fig. 3. In the subsequent

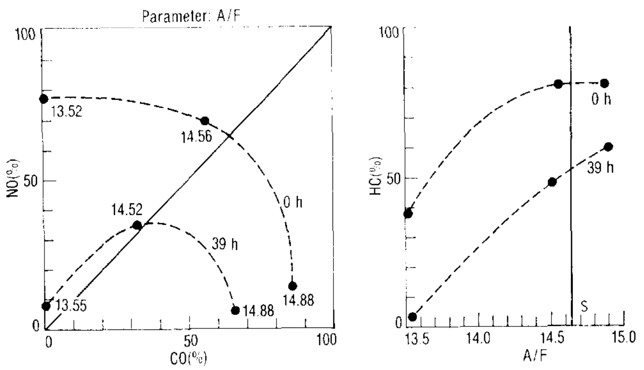

FIG. 4. Performance of a coimpregnated Pt/Rh catalyst with both Rh and Pt near the outer pellet surface. Dynamometer tests, catalyst A.

parts of this paper, we will explore the role of subsurface Rh impregnation depth in affecting catalyst activity and poison resistance, and the roles of Ce and Pd addition.

RESULTS AND DISCUSSION

a. *Effects of Subsurface Rh Location*

The catalysts discussed here are listed in Table 1. Support A (Table 2) was employed. Fuel a was used in the aging process (Table 4). The experiments were conducted in the 1000-cm^3 reactor, attached to the static engine dynamometer system which was described in section c of the experimental part.

Figure 4 shows catalyst A which was coimpregnated by Pt and Rh. IMMA scans indicated that both Pt and Rh have their highest concentrations near the pellet surface, rapidly decreasing with distance into the pellet. In Fig. 4, the NO conversion is plotted as a function of CO conversion at various selected values of A/F, as indicated on the curves. As we will see, such plots have a considerable utility in allowing an easy visualization of the complex events which take place in stoichiometric catalysis.

Observing Fig. 4, we note that the fresh catalyst has its highest NO conversion at rich stoichiometries. The crossing of the curves with the diagonal shows the so-called crossover point, where the CO conversion equals the NO conversion.

After 39 hr of aging on fuel a, both the CO and NO conversions decreased. However, while the lean CO (and HC) conversions retained a good fraction of their initial value, the rich NO conversion essentially disappeared, because the minute

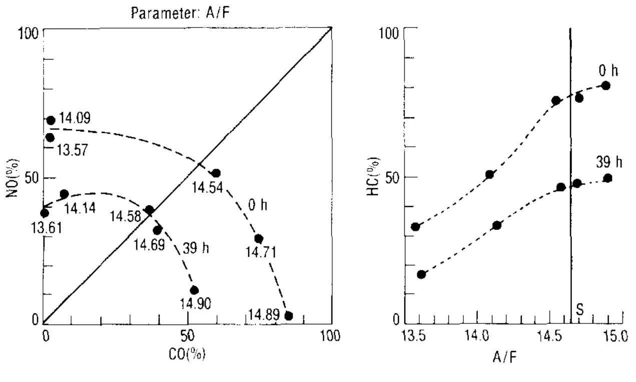

FIG. 5. Performance of a Pt/Rh catalyst (Rh 60 μm subsurface). Dynamometer tests, catalyst B.

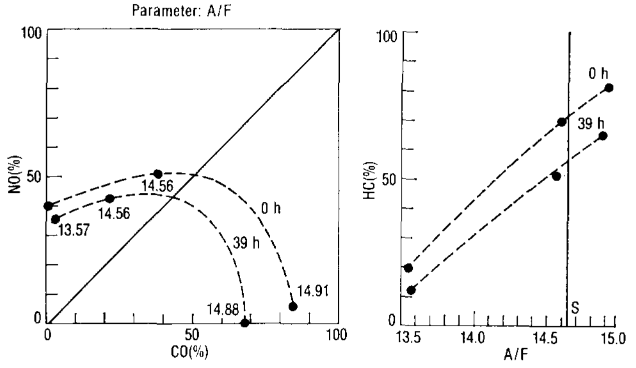

FIG. 6. Performance of a Pt/Rh catalyst (Rh 120 μm subsurface). Dynamometer tests, catalyst C.

quantities of Rh were exposed to the poisons. Note that the NO conversion of the aged catalyst is much higher close to the stoichiometric point than at the rich end of the scale, most likely due to the fact that not all the Pt has been poisoned, and that Pt is able to reduce NO near the stoichiometric point, but not under rich conditions, as discussed before.

Let us now investigate what happens if the catalyst is prepared in such a way that its Rh is buried 60 μm below the pellet surface, while the Pt is left in the outer shell (catalyst B, Fig. 5). The fresh CO (and HC) performance at lean A/F remained unchanged: This shows that the bulk of the oxidizing performance is indeed provided by Pt. However, the fresh rich (diffusion-limited) NO conversion is reduced somewhat when compared with the previous case. Obviously, this was caused by the increased diffusion path length due to subsurface Rh impregnation.

While subsurface Rh impregnation reduced the initial NO conversion, it has a striking effect upon preserving the Rh during the aging process, as a comparison of Figs. 4 and 5 reveals. Indeed, while the surface Rh catalyst had only 9% NO conversion at the rich end after aging, the 60-μm subsurface catalyst had about 40%, a very large improvement.

We may at this point conclude that while subsurface Rh impregnation reduced the initial performance of a catalyst, it appears to protect its Rh content from poisoning and thus it improves the poison resistance; that is, initial activity is being sacrificed for better durability. (Figure 6, which shows catalyst C with Rh about 120 μm below the surface, lends further support to this mechanism.)

b. *Effects of Ce and Pd Addition*

Both the effects of Ce and Pd could be explored by comparing the performance of the following four catalysts (Table 1):

D	(Pt/Rh)
E	(Pt/Rh//Ce)
F	(Pt/Rh/Pd)
G	(Pt/Rh/Pd//Ce)

The effect of Ce on the static performance of the Pt/Rh catalysts is minimal. However, the fresh performance in the cycled dynamometer test improves significantly upon Ce addition. An inspection of Fig. 7 reveals that the NO and CO conversions within an A/F bracket of, e.g., ±0.20 are higher for the Pt/Rh//Ce catalyst than for the Pt/Rh catalyst. In addition, an improvement in both CO and NO conversions is observed in the proximity of the stoichiometric A/F (marked by S) in these cycled experiments, as a result of Ce addition.

The difference between static and cycled experiments [that is, Ce addition does not

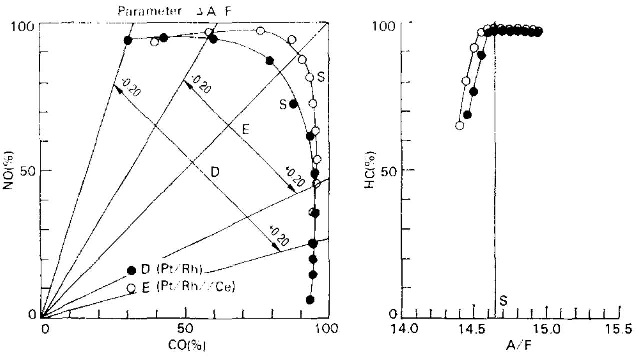

FIG. 7. Effects of Ce on the cycled dynamometer performance of Pt/Rh catalysts.

have any effect on the static conversions (Fig. 8) but improves the conversions in a cycled test (Fig. 7)] might well be due to a surface storage effect, even though it is not entirely clear as to which component or components are being stored and slowly released during the A/F transients.

Ce addition also influenced the cycled performance of the Pt/Rh/Pd catalyst, in a manner not too different from its effects on the Pt/Rh catalyst discussed above.

Let us now cross-reference our four catalysts and discuss the effects of Pd addition by comparing their activity both in the absence and in the presence of Ce.

The CO and NO conversions of the Pt/Rh catalyst on the static dynamometer are only slightly affected by Pd addition (slight improvement in static fresh HC conversion). The effect of Pd is also slight on the cycled dynamometer performance: We noted a slight A/F window improvement on the lean side, and a slight HC conversion improvement on the rich side.

More interesting (and more complex) is the effect of Pd addition on Pt/Rh//Ce. In the static dynamometer experiments, no effects on fresh CO and NO conversions, and a beneficial effect on the fresh HC conversion were observed, in agreement with the Pt/Rh catalysts. After static aging, the Pt/Rh/Pd//Ce catalyst had a better CO–NO crossover point and essentially unchanged rich NO, and lean CO and HC conversions when compared to the Pd-free counterpart.

The effects of Ce and Pd on Pt/Rh catalysts were also investigated using a

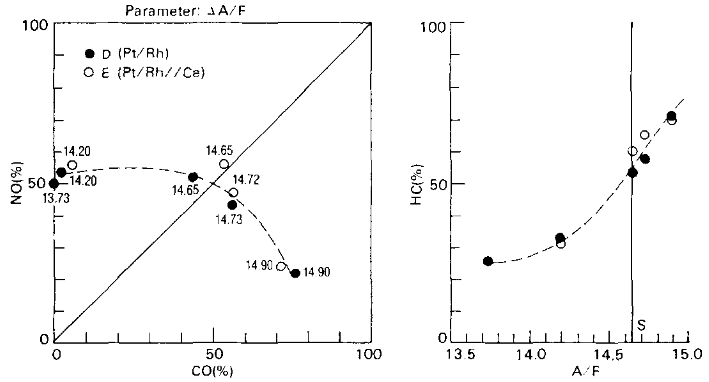

FIG. 8. Effects of Ce on the initial performance of Pt/Rh catalysts in the static accelerated dynamometer test.

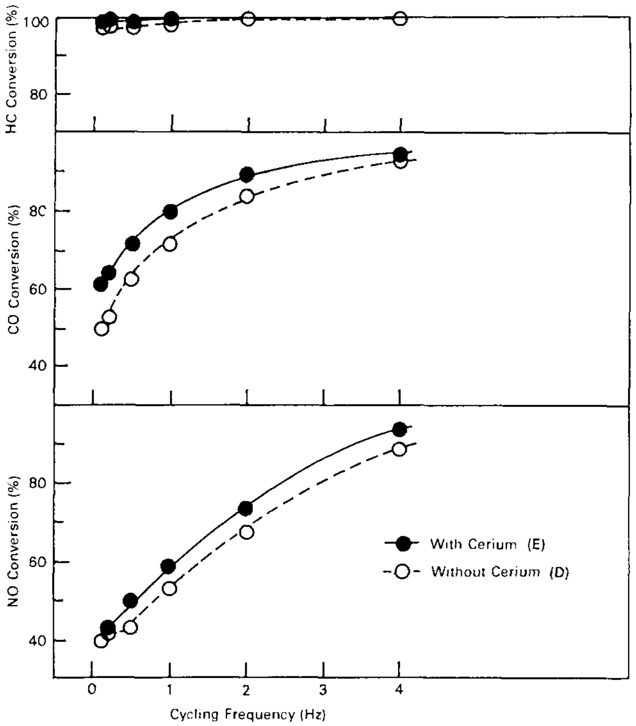

FIG. 9. Effects of Ce on performance of Pt/Rh in a laboratory feedstream cycled at variable frequency.

cycled feedstream in the laboratory reactor. The cycled dynamometer data were taken at a constant frequency (1 Hz), while the cycled laboratory experiments allowed us to investigate various frequencies, covering the range of 0.1 Hz to about 6 Hz. Certain exhaust components which influence catalyst performance (SO_2, P, halides) are absent from the laboratory feedstream, so extrapolations must be done with caution. Nevertheless, the laboratory testing brought out some interesting features of these experimental catalysts.

Figure 9 shows how Ce affected the laboratory performance of our fresh Pt/Rh catalysts (E vs D) as the cycling frequency was varied from 0.1 to 4 Hz. Both CO and NO conversions were strongly dependent upon the frequency of A/F oscillation. The highest conversions occurred at the highest frequency; the feedstream at the limit of very high frequency is simply a constant flow of stoichiometric composition. It is clear that catalyst efficiencies during cycling at 1 Hz, a typical frequency in catalyst evaluation practice, are significantly lower than those measured in a steady flow situation. Ce improved both CO and NO conversion levels at all frequencies. Because propylene (HC) conversions were so high in our tests, it was difficult to distinguish differences between fresh catalysts.

These same Pt/Rh and Pt/Rh//Ce catalysts were reexamined in the laboratory after 20 hr of aging on the static accelerated dynamometer (Fig. 10). The exhaust exposure decreased the effectiveness of both catalysts for converting HC, CO, and NO. The sample with Ce remained more effective for CO conversion than the sample without Ce, but HC and NO conversions were decreased by Ce addition in the aged samples.

Ce addition to a fresh Pt/Rh/Pd cata-

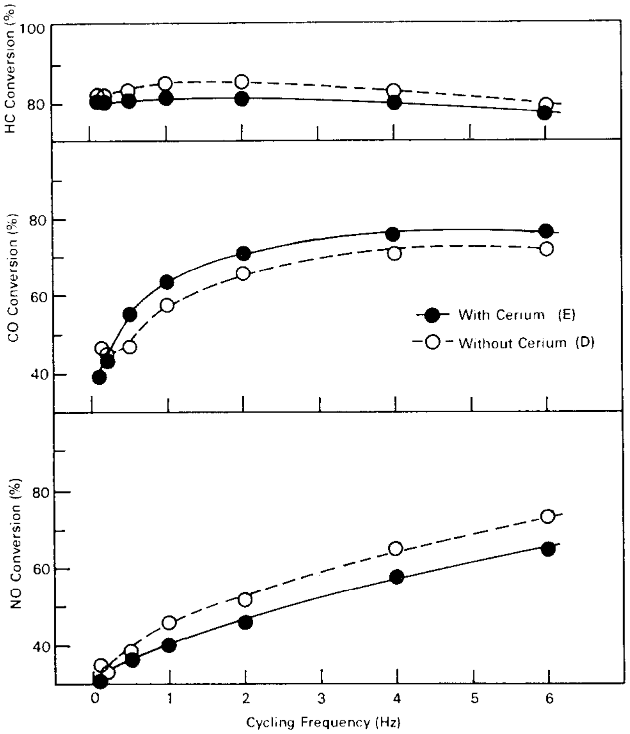

FIG. 10. Effects of Ce on Pt/Rh after 20-hr exhaust exposure (Fuel b).

lyst gave results much like those just discussed for the Pt/Rh catalyst (Fig. 9). CO and NO conversions improved, and both samples showed marked response to cycling frequency. For the samples aged 20 hr in the accelerated static dynamometer test, the primary benefit of Ce addition was in CO conversion. HC conversion was slightly higher for Pt/Rh/Pd//Ce than for Pt/Rh/Pd, but the NO conversion was almost independent of whether or not Ce was present in the aged samples.

Palladium's contributions can be extracted from cross-comparisons of the cycled laboratory results on the Pd-free and Pd-containing catalysts. The fresh Pt/Rh and Pt/Rh//Ce catalysts showed a slight increase in NO conversion when Pd was added, and these increases were retained after aging. Overall, Pd had less

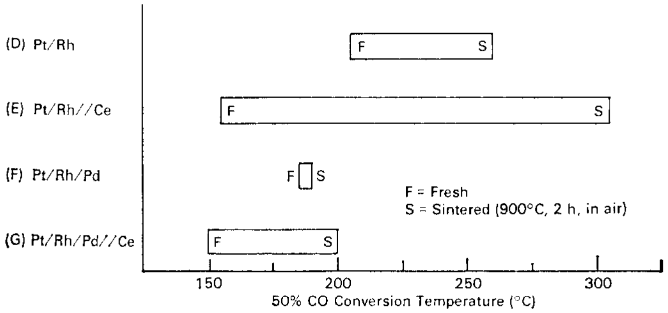

FIG. 11. Effects of Ce and Pd on the lightoff of fresh and thermally sintered catalysts (laboratory bench tests).

TABLE 5

Vehicle FTP Tests on Fresh Catalysts (Closed-Loop Vega, Vacuum Modulated Carburetor)

Catalyst	Overall test efficiency (%)		
	HC	CO	NO
D (Pt/Rh)	80	64	72
E (Pt/Rh//Ce)	80	74	75
F (Pt/Rh/Pd)	78	67	73
G (Pt/Rh/Pd//Ce)	84	79	83

effect on catalyst performance than Ce did in these cycled laboratory tests with the reactor operated at a steady-state temperature of 550°C.

In addition to their warmed-up performance, though, automotive catalysts are also judged by their ability to light off at a low temperature. To test their lightoff performance, the catalysts were investigated in a laboratory reactor under oxidizing conditions. The feedstream consisted of 1.5% O_2, 0.3% CO, 0.025% propylene, 10% CO_2, 10% H_2O, and N_2 to 100% (all by vol), and the temperature was gradually increased (10°C/min). The space velocity was 85,000 hr^{-1} (20°C, 1 atm).

Figure 11 compares the 50% CO conversion temperatures of our four catalysts (Table 1), before and after thermal exposure (900°C, 2 hr in air). The results can be summarized very briefly: Ce enhances the initial lightoff performance (due to increasing the dispersion of the metals, as separate experiments indicated), while Pd primarily enhances the lightoff performance after thermal exposure, due to the thermal stability of its dispersion (it appears that Ce degrades the thermal stability of Pt). Consequently, both Ce and Pd seem to have a beneficial overall effect on the performance of Pt/Rh catalysts.

The fresh performance of the four catalysts was also evaluated in a 4261-cm^3 converter attached to a vehicle (section e in the experimental part). The FTP emissions (test efficiencies) are listed in Table 5. The simultaneous addition of Pd and Ce to the low-Rh catalyst significantly improved the fresh HC, CO, and NO conversions when compared with any other combination. (These car data include both cold-start and hot conversion performance as dictated by the FTP procedure.)

The above results are encouraging in that they indicate the possibility of preparing improved low-Rh catalysts. Real-time engine dynamometer and vehicle aging tests are required, however, to prove their durability in actual automobile service.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions of S. A. Ausen, T. S. Chou, D. Fournier, J. E. Hochlowski, P. J. Mitchell, A. C. Ottolini, M. Perry, N. M. Potter, R. W. Richmond, R. M. Sinkevitch, E. A. Sloan, H. E. Vergosen (General Motors Research Laboratories), and D. E. Achey, R. E. Bedford, M. Berg, W. M. Wang (AC Spark Plug Division, General Motors Corporation). The NO–CO cross-plots were originally suggested by R. Aris. The IMMA measurements were carried out by the Applied Science Laboratories.

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