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Platinum and Palladium Addition to Supported Rhodium Catalysts for Automotive Emission Control

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Simultaneous catalytic control of the three major pollutants in automobile exhaust requires both reduction of nitric oxide and oxidation of carbon monoxide and hydrocarbons. A supported rhodium catalyst with low loading (0.002 wt% Rh) was found to have good activity for converting nitric oxide to nitrogen in a laboratory feedstream, but its oxidation activity was inadequate. Addition of platinum or palladium improved the oxidation activity. However, it was found that, compared to rhodium alone, these two-metal combinations (Pt–Rh or Pd–Rh) form more ammonia under reducing conditions and decrease nitric oxide conversion under oxidizing conditions. Both of these undesired effects were circumvented by depositing the added metals on separate support beads. The rhodium catalyst was located in the front of the catalyst bed and was followed by a second layer of pellets containing the platinum or palladium. Evaluations in engine exhaust remain to be done, since laboratory results are not conclusive indicators of actual emission-control performance.

INTRODUCTION

An automotive emission-control system must remove nitrogen oxides (NO_x), hydrocarbons (HC), and carbon monoxide (CO) from the exhaust. Beginning with 1975-model automobiles, most manufacturers have used catalytic oxidation to satisfy CO and HC emission regulations; NO_x specifications have been met with engine modifications. Such modifications may not, however, be sufficient to comply with future requirements; so the catalytic approach is being considered for control of all three major pollutants. This means that, in addition to the oxidation of CO and HC presently being catalyzed, catalytic reduction of nitric oxide to nitrogen may also be required.

The need to carry out both oxidation and reduction reactions in the same feedstream leaves the control system designer with a choice of two basic schemes (*1*). One is to operate a fuel-rich engine to provide an oxygen-deficient (reducing) exhaust in which nitric oxide reduction (by CO, HC, and H_2) can be catalyzed. Then air is pumped into the exhaust as it passes into a second catalyst bed for oxidizing the remaining CO and HC. The alternative control scheme is to operate the engine with the stoichiometrically correct air–fuel ratio to provide exhaust with just the proper balance of oxidizing agents (O_2, NO) and reducing agents (CO, HC, H_2). An ideal catalyst then could equilibrate the entire mixture and eliminate all three pollutants simultaneously (hence, the term "three-way catalyst").

This latter scheme has the advantage of using a single catalyst bed, and stoichiometric engine operation gives better fuel economy than the rich operation required for the dual-bed approach. It does, however, require a precise feedback-controlled

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fuel-metering system governed in part by an oxygen sensor in the exhaust stream. The continual sensing and readjustment of the air–fuel ratio causes the exhaust to fluctuate about the stoichiometric composition (*2*). This places additional demands upon the three-way catalyst; it must maintain its effectiveness on both the rich and lean sides of the stoichiometric point.

Much of the early work on potential NO_x control catalysts focused on the rich operating conditions encountered in the dual-bed approach. In the absence of oxygen, ruthenium is the most effective metal for reducing NO selectively to N_2 rather than NH_3 (*3, 4*). However, small amounts of oxygen are detrimental to ruthenium catalysts (*5–10*). Certain base-metal oxides have been shown to stabilize supported ruthenium against oxidation (*9, 10*), but the long-term viability of such systems remains uncertain (*9–11*). Rhodium is preferred for the three-way application where oxygen is present in the reactant stream (*5–8, 12–14*). The presence of oxygen improves the N_2 selectivity of platinum catalysts too (*15*); but rhodium is still a more effective catalyst for three-way control (*13*). A direct comparison of iridium (*16*) with rhodium has not been reported.

Gandhi *et al.* have recently described the properties required of a three-way catalyst (*17*). One important property is the ability to reduce NO selectively to N_2 (not NH_3) under both rich and slightly lean operating conditions. A second requirement is oxidation activity sufficient to control CO and HC emissions without the need for a separate oxidizing converter system. The first function, NO control in the presence of oxygen, can be carried out with rhodium supported on alumina (*5–8, 12–14*). However, rhodium is 15–20 times more scarce than platinum in the world; so feasible loadings for widespread automotive application are quite low. For this reason, additional catalytic components are sometimes included to enhance oxidation performance (*17*).

In the work reported here, we have explored the effects of adding platinum and palladium to improve the oxidizing capacity of a rhodium catalyst. The results have both scientific and practical importance; they have increased our understanding of three-way catalysis over combined metals and have pointed a way toward possible improvements in converter systems for emission control.

METHODS

All catalysts were prepared by impregnating alumina spheres (Kaiser low-density Al_2O_3, 3 mm in diameter, bulk density $\sim$0.55 g/cm^3) to incipient wetness with a solution of the appropriate metal chlorides ($RhCl_3 \cdot 4H_2O$, ROC/RIC; 5% solution of $PdCl_2$, Matheson, Coleman, and Bell; 10% solution of $H_2PtCl_6 \cdot 6H_2O$, Matheson, Coleman, and Bell). After drying overnight at ambient temperature, the beads were heated in flowing air for 4 hr at 100°C and then for 4 hr at 500°C. The thermal aging treatments were carried out by placing the sample for 24 hr in a muffle furnace previously heated to 900°C.

Catalysts were tested for three-way performance at a fixed temperature of 538°C after first stabilizing the sample in the reducing (i.e., without O_2) reactant feedstream at 650°C. The apparatus has been described in detail elsewhere (*18*). The feed gas blended to simulate the typical mole percentages in the exhaust (0.1% NO, 1% CO, 0.3% H_2, 10% CO_2, 10% H_2O, 0–1% O_2, remainder N_2) was passed through 15 cm^3 of the sample at a 38,000-hr^{-1} space velocity. By using different inlet O_2 levels, we covered the region from "rich" to "lean" operation; the stoichiometric O_2 concentration for the standard feed was 0.6%. Outlet concentrations were measured after the reactor had stabilized at each new inlet O_2 level. [Note: A change of 0.1% in exhaust O_2 concentration corresponds to approximately 0.08 air/fuel-ratio unit (*19*).] Results of our three-way catalyst evaluations are then reported as reactor outlet concentrations versus inlet O_2 concentration. These laboratory results are not directly translatable into converter performance values, but they do show which approaches are worthy of further testing.

Although CO conversion is measured as part of the laboratory three-way evaluation, the high catalyst temperature in that test minimizes the differences observed between the oxidation activities of the various samples. For this reason, oxidizing capabilities of our catalysts were measured in equipment much like the three-way test reactor, but with a feedstream chosen to compare specifically the oxidation performance (i.e., excess oxygen). For most comparisons, the feedstream contained 2% CO, 0.05% propylene, 2% O_2, 10% CO_2, and 10% H_2O in a nitrogen background. It was passed through 10 cm^3 of catalyst at a space velocity of 85,000 hr^{-1} as the temperature was increased from ambient to ~650°C in about 45 min. Oxidation of CO and propylene to CO_2 and H_2O was monitored as a function of the catalyst temperature. In certain experiments (identified in the text) it was important to use the same catalyst bed in both the three-way and oxidation evaluations, so a volume of 15 cm^3 was used for both tests. The oxidation feedstream in these cases was 0.3% CO, 0.025% propylene, 1.5% O_2, 10% CO_2, and 10% H_2O in a nitrogen background flowing at a space velocity of 57,000 hr^{-1}.

RESULTS AND DISCUSSION

Rhodium Alone

A three-way catalyst must promote both NO removal (by reaction with CO, HC, or H_2) and CO and HC removal (by reaction with O_2, NO, or H_2O). In the case of precious-metal catalysts, availability of the active component imposes an additional constraint. Rhodium, for example, is 15–20 times less plentiful than platinum in the mines of South Africa. Obviously, we are interested in lowering metal loadings to the fullest extent compatible with acceptable performance.

To determine the sensitivity of performance to metal loading we tested Rh/Al_2O_3 catalysts at two loadings, 0.1 and 0.002 wt%. The latter is a reasonable target for large-scale automotive use. The results of our laboratory "three-way" evaluation are depicted in Fig. 1. The curves are typical of Rh; NH_3 is formed as a product of NO reduction at the lowest O_2 levels and disappears as O_2 is added. Once the stoichiometric O_2 concentration (0.6%) is exceeded, the NO is not reduced as efficiently over the catalyst. Surprisingly, a 50-fold decrease in Rh loading showed little effect on NO removal efficiency and NH_3 formation.

Various Rh loadings were also examined for oxidation performance, the second criterion described above for a three-way catalyst. The results are expressed in Fig. 2 as percentage conversions of the standard reactant stream at 300°C. In contrast to the reduction of NO, there is a marked loss in oxidation efficiency in going to the low metal loadings of practical interest. It should be pointed out that rhodium is not inherently a poor oxidation catalyst; on the

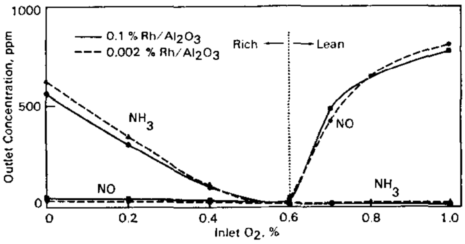

FIG. 1. NH_3 formation and NO appearance over fresh rhodium catalysts at two loadings.

contrary, its activity compares favorably with platinum and palladium (*20*). The drawback with rhodium is simply that availability limits the loading, and the low loading limits oxidation performance.

Combined Metals: Oxidation

Because platinum and palladium are effective oxidation catalysts and are in larger supply than rhodium, it seems reasonable to use one of these metals in combination with rhodium to provide a three-way catalyst with improved oxidation performance (*17*). We prepared such two-metal samples with loadings chosen to approximate commercial viability, that is, 0.05 wt% Pt, 0.02 wt% Pd, and 0.002 wt% Rh. The oxidation evaluation was done on thermally aged samples because the high activity of fresh catalysts makes them nearly indistinguishable in our standard oxidation test and because the thermal treatment is a conveniently reproducible laboratory procedure for aging samples.

As expected, chemisorption uptakes decreased as a result of the 900°C exposure. A fresh 0.05% Pt/Al_2O_3 sample adsorbed 1.01 μmol of H_2/g, while the sintered one adsorbed 0.08 μmol of H_2/g. We were not able to determine uptakes reliably on 0.002 wt% Rh/Al_2O_3, but fresh and aged Rh at the 0.1% level took up 1.1 and 0.1 μmol of H_2/g, respectively, after being exposed to the 650°C reaction conditions. Of the samples for which catalytic activities are reported here, only the 0.05 wt% Pt–0.002 wt% Rh sample was characterized using chemisorption. It took up 1.82 μmol of CO/g fresh and 0.08 μmol of CO/g after thermal aging. With two metals present, and given the uncertainties of chemisorptions on rhodium (*21*), the interpretation of chemisorption values remains obscure.

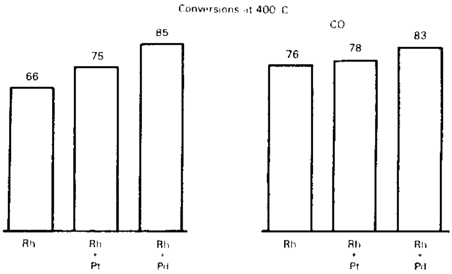

FIG. 3. Oxidation activity of various metal combinations. All samples aged 24 hr at 900°C in air.

Figure 3 shows that, indeed, Pt or Pd combined with Rh on a support enhances the conversion of HC and CO in the oxidation test. The enhancement is greater for Pd than for Pt; that reflects the greater thermal stability of Pd in the oxidizing atmosphere used for aging (*22*).

Combined Metals: NH_3 Formation

These same two-metal catalysts were also evaluated in our laboratory three-way simulation procedure. Earlier experiments had shown that either Pt or Pd alone forms significant quantities of NH_3 on the rich side of the stoichiometric point (*13*). That observation was also made using a Pt

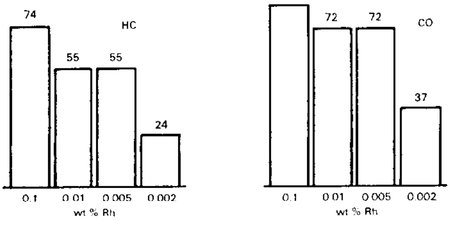

FIG. 2. Oxidation activity at various rhodium loadings.

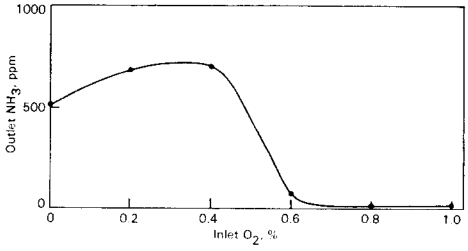

FIG. 4. NH_3 formation over fresh platinum in three-way test.

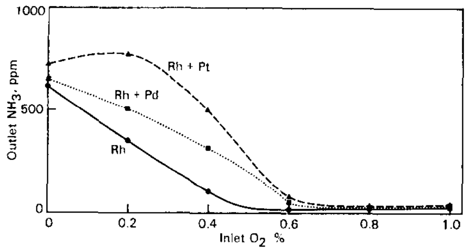

FIG. 5. NH_3 formation over fresh three-way catalysts.

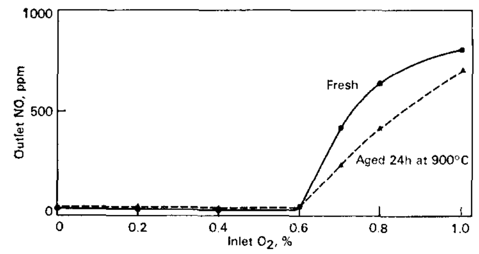

FIG. 7. Effect of thermal aging on lean-side NO control by rhodium.

catalyst at the 0.05 wt% loading chosen for this study, as shown in Fig. 4. This ammonia-forming property of Pt and Pd catalysts, if carried over to the Pt–Rh and Pd–Rh combinations, would be an undesirable feature of the two-metal approach.

NH_3 formation over the combined catalysts in the laboratory three-way test is compared to the NH_3 formed over Rh alone in Fig. 5. The two-metal systems produce considerably more NH_3 than Rh alone, and the NH_3 persists in significant amounts over the entire range of rich operation ($<0.6\%$ O_2). This may simply be a consequence of the more than tenfold excess (on an atomic basis) of platinum or palladium over rhodium in the two-metal catalysts. Rhodium by itself catalyzes NH_3 removal under these experimental conditions, particularly with O_2 present (*13*); that may explain why Rh + Pt forms less NH_3 than Pt alone as the O_2 level is increased (cf. Figs. 4 and 5). We cannot, however, discount the possibility that, in the combined system, a Rh–Pt alloy is responsible for the NH_3 values intermediate between those of the pure metals.

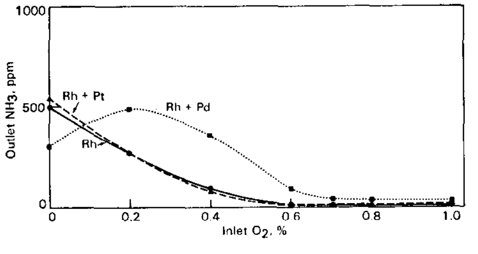

FIG. 6. NH_3 formation over aged three-way catalysts.

Pretreatment in air for 24 hr at 900°C causes interesting changes in the ammonia generation curves of the various catalysts. Figure 6 shows that, in each case, NH_3 formation is decreased relative to the fresh catalyst results (Fig. 5). The most striking feature of Fig. 6, though, is the coincidence of the "Rh + Pt" and the "Rh" lines. The implication is that the platinum has sintered to the extent that it is no longer effective in the reducing reactions; so the NH_3 curve is governed solely by the Rh characteristics. Alloying still cannot be ruled out, however, because the aging treatment might have caused surface rearrangements to yield rhodium-like catalytic behavior. In fact, rhodium enrichment at the surface of platinum–rhodium foils oxidized at high temperature has been documented using X-ray photoelectron spectroscopy (*23*). Palladium, because it does not sinter as readily as platinum, retains appreciable activity for NH_3 formation even after thermal aging.

Combined Metals: Lean-Side NO Control

In the Introduction, it was noted that a three-way catalyst must be effective in removing CO, HC, and NO at lean as well as rich air/fuel ratios. The difficult species to control on the lean side ($>0.6\%$ O_2 in our experiments) is NO, as depicted in Fig. 7. Note that with the fresh Rh catalyst the NO reappears rapidly once the inlet

O_2 level exceeds the stoichiometric amount. The unexpected observation with the Rh/Al_2O_3 catalyst was that the *thermal aging actually improved lean-side NO control;* that is, as the inlet O_2 concentration increased the concentration of NO at the reactor outlet was lowered considerably relative to the fresh catalyst. We shall return to this observation shortly, but, first, let us examine the NO curves for the thermally aged Rh–Pt and Rh–Pd catalysts displayed in Fig. 8.

Here again there are marked differences among the samples, with Rh–Pd losing NO control quickly in the presence of only a slight excess of O_2. As in the case of NH_3 formation, the aged Rh–Pt sample is essentially equivalent to the Rh alone.

The data just presented, when combined with the measurements of oxidation activity shown earlier, provide a key to understanding the connection between some of the various reactions which occur in three-way catalysts. Because it can react with either NO or O_2, carbon monoxide plays a pivotal role in determining the efficiency of NO removal. An effective three-way catalyst must promote the CO–NO reaction in the presence of O_2, and this criterion has made rhodium a common choice for three-way control (*8, 9, 13, 17*). However, the addition of Pt or Pd to promote the oxidation reactions (e.g., CO–O_2) upsets the overall selectivity for NO removal.

There is apparently a delicate balance which determines the amount of NO consumed by the reducing agents (CO, H_2). Since oxygen reacts readily with the CO and H_2, it tends to regulate the quantity of these reactants available for NO reduction. On the rich side of the stoichiometric point, the reducing agents are in excess, so both NO and O_2 are virtually eliminated. On the lean side, however, the reducing species become the limiting reactants, and the partitioning of these species between NO and O_2 determines the effectiveness of NO control under lean conditions. The results in Figs. 7 and 8 indicate that the catalysts with higher oxidation activities, as measured in our oxidation test, are less efficient for converting NO on the lean side, presumably because they catalyze CO and H_2 oxidation by O_2 at the expense of NO reduction reactions. Thus, the partitioning of the reducing agents between NO and O_2 is influenced by the oxidation activity of the catalyst. Details of the chemistry involved in these observations and the reason why NO competes more favorably with O_2 in reactions over rhodium after the catalyst is thermally aged are subjects of ongoing studies in our laboratories.

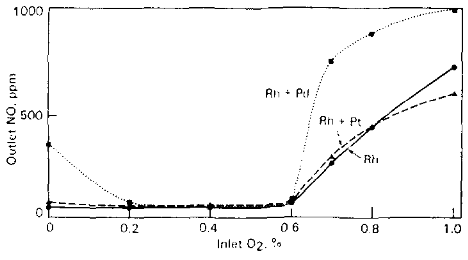

FIG. 8. Effect of added metals on lean-side NO control (thermally aged catalysts).

Combined Metals: A New Approach

We have described how adding Pt or Pd to Rh has advantages and disadvantages; the oxidation activity is certainly improved, but control of NH_3 and lean-side NO is sacrificed. We can, however, arrange the conditions to maximize the advantages and minimize the disadvantages of these two-metal systems. Let's consider what we basically want from each metal.

Rhodium's primary function is to reduce NO to N_2 selectively by reaction with CO, H_2, or HC. This is, of course, enhanced by high concentrations of the reducing agents.

Platinum's (or palladium's) role is to eliminate the reducing agents (CO, H_2, HC) by reacting them with oxygen. This is in conflict with the role of Rh given above. An undesirable characteristic of Pt and Pd

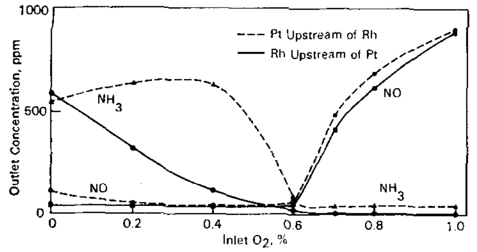

FIG. 9. NH_3 formation and NO appearance when metals are separated in the catalyst bed (fresh catalysts).

is NH_3 formation, a process aided by high NO and reducing agent concentrations.

Notice that the rhodium-catalyzed reactions are best done under the reactor inlet conditions, where reducing agent concentrations are highest. Platinum and palladium, on the other hand, should be put at the reactor outlet where lowered concentrations will minimize the potential for NH_3 formation. Also, the oxidation reactions over Pt and Pd won't consume the reducing agents before they have had a chance to react over the Rh catalyst.

The effectiveness of this simple idea of separating the metals on different support beads in the reactor is depicted in Fig. 9 for Rh and Pt. The total catalyst volume is 15 cm^3 as before, comprising 7.5 cm^3 each of 0.005 wt% Rh/Al_2O_3 and 0.1 wt% Pt/Al_2O_3. Thus, the total metal content of the reactor is the same as we used for the combined catalysts discussed previously. To be sure of observing only the effects of catalyst bed geometry, we compared the Rh upstream–Pt downstream combination with the same catalysts in the inverted configuration. Data for the two metals on the same support (Fig. 5) and for the two catalysts stirred together fall between the two extremes plotted in Fig. 9. For the reasons discussed above, NH_3 formation is lowered considerably when Pt is placed downstream of Rh, rather than at the reactor inlet where high NO concentrations prevail.

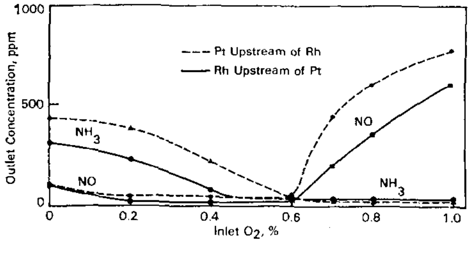

FIG. 10. NH_3 formation and NO appearance when metals are separated in the catalyst bed (catalysts aged 24 hr at 900°C).

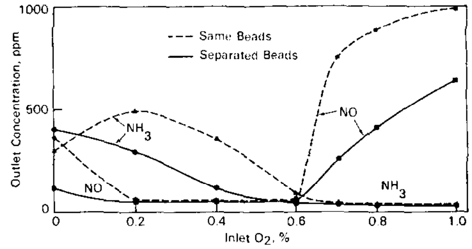

FIG. 11. Comparison of rhodium + palladium on separated beads versus both metals on the same beads (thermally aged catalysts).

Earlier we saw that thermal aging virtually eliminated the effect of Pt addition on the NH_3 formation and NO removal characteristics of a Rh catalyst (Figs. 6 and 8). That is not the case for the separated metals. Figure 10 shows that, even after aging, there is a significant effect of bed geometry, indicating that the platinum still retains at least a small amount of activity under these conditions. Like the fresh sample, the aged Rh upstream configuration makes less NH_3 (cf. Fig. 6) and has better lean NO control (cf. Fig. 8) than aged Pt–Rh on the same beads.

Perhaps the most striking evidence of the benefits of separating the metals is seen in experiments using rhodium and palladium. We noted above that, even after thermal aging, the Rh–Pd catalyst made significant amounts of NH_3 under rich conditions and quickly lost NO control under lean conditions. These data appear in Fig. 11 along with the results obtained with Rh/Al_2O_3 upstream of Pd/Al_2O_3. As before, the metal loadings on the separated beads were adjusted to be comparable to those on the combination catalyst. The curves for the separated bed (solid lines) are practically identical to those for aged Rh alone, showing that the drawbacks of adding Pt and Pd to a three-way control system can be overcome by careful attention to the catalyst configuration.

Having eliminated the major drawbacks of Pt and Pd addition, we needed to confirm that we hadn't eliminated the oxidation improvement in the process. Each oxidation evaluation was carried out using the same catalyst bed as used for the three-way evaluation; thus, the volume was 15 cm^3 rather than the 10 cm^3 typically used in the standard oxidation test. At the same time, we changed the oxidizing feedstream in order to simulate more nearly the steady-state exhaust composition of current engines (0.3% CO, 0.025% propylene, 1.5% O_2, 10% CO_2, 10% H_2O in N_2). The two-metal systems had the Rh catalyst upstream of the Pt or Pd catalyst, as dictated by the three-way evaluations just discussed. The results for the separated beds and for Rh alone, all thermally aged, are shown in Fig. 12. Clearly, the oxidation activity is improved with the stacked catalysts, particularly for HC oxidation.

SUMMARY

In laboratory testing, supported fresh rhodium catalysts at the low loadings of practical interest appear to have adequate activity for converting NO to N_2 but not for oxidizing CO and HC. Addition of platinum or palladium to the rhodium catalyst improves its oxidation performance but increases the amount of ammonia formed on the rich side of the stoichiometric point. The higher oxidation activity also causes more rapid loss of nitric oxide control as the reactant mixture becomes leaner than stoichiometric (i.e., excess O_2).

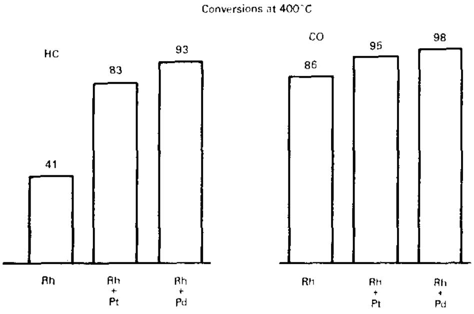

FIG. 12. Oxidation performance of two-metal systems on separated pellets. All samples aged 24 hr at 900°C in air.

By depositing the platinum or palladium on different pellets from the rhodium, we have been able to obtain the enhanced oxidation activity of the two-metal catalysts without sacrificing selectivity or activity for NO reduction to N_2. The key feature of this work is the recognition that the correct choice of configuration of the catalytic components will put each in the most favorable environment for its intended function. The result is a significant improvement over catalyst beds with the active components distributed uniformly throughout the reactor.

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REFERENCES

1. Klimisch, R. L., and Komarmy, J. M., *in* "The Catalytic Chemistry of Nitrogen Oxides" (R. L. Klimisch and J. G. Larson, Eds.). Plenum Press, New York, 1975.
2. Zechnall, R., Baumann, G., and Eisele, H., Paper No. 730566 presented at Society of Automotive Engineers Meeting, Detroit, Mich., 1973.
3. Kobylinski, T. P., and Taylor, B. W., *J. Catal.* **33**, 376 (1974).
4. Klimisch, R. L., and Taylor, K. C., *Environ. Sci. Technol.* **7**, 127 (1973).
5. Bernhardt, W. E., *in* "The Catalytic Chemistry of Nitrogen Oxides" (R. L. Klimisch and J. G. Larson, Eds.). Plenum Press, New York, 1975
6. Mannion, W. A., Aykan, K., Cohn, J. G., Thompson, C. E., and Mooney, J. J., *in* "Catalysts for the Control of Automotive Pollutants" (J. E. McEvoy, Ed.); *Advan.*

Chem. Ser. **143**. American Chemical Society, Washington, D.C., 1975, p. 1.

7. Ashmead, D. R., Campbell, J. S., Davies, P., and Farmery, K., Paper No. 740249 presented at the Society of Automotive Engineers Congress, Detroit, Mich., 1974.
8. Bauerle, G. L., Service, G. R., and Nobe, K., *Ind. Eng. Chem. Prod. Res. Develop.* **11**, 54 (1972).
9. Shelef, M., and Ghandhi, H. S., *Platinum Metals Rev.* **18**, 2 (1974).
10. Kobylinski, T. P., Taylor, B. W., and Young, J. E., Paper No. 740250 presented at Society of Automotive Engineers, Congress, Detroit, Mich., 1974.
11. Clausen, C. A., and Good, M. L., *J. Catal.* **46**, 58 (1977).
12. Ohara, T., *in* "The Catalytic Chemistry of Nitrogen Oxides" (R. L. Klimisch and J. G. Larson, Eds.). Plenum Press, New York, 1975.
13. Taylor, K. C., *in* "The Catalytic Chemistry of Nitrogen Oxides" (R. L. Klimisch and J. G. Larson, Eds.). Plenum Press, New York, 1775.
14. Meguerian, G. H., and Rakowsky, F. W.,Paper No. 750417 presented at Society of Automotive Engineers Meeting, Detroit, Mich., 1975.
15. Jones, J. H., Kummer, J. T., Otto, K., Shelef, M., and Weaver, E. E., *Environ. Sci. Technol.* **5**, 790 (1971).
16. Tauster, S. J., and Murrell, L. L., *J. Catal.* **41**, 192 (1976).
17. Gandhi, H. S., Piken, A. G., Shelef, M., and Delosh, R. G., Paper No. 760201 presented at Society of Automotive Engineers Congress, Detroit, Mich., 1976.
18. Klimisch, R. L., and Barnes, G. J., *Environ. Sci. Technol.* **6**, 543 (1972).
19. D'Alleva, B. A., "Procedure and Charts for Estimating Exhaust Gas Quantities and Compositions." GMR Report 372, 1960.
20. Taylor, K. C., *Ind. Eng. Chem. Prod. Res. Develop.* **15**, 264 (1976).
21. Wanke, S. E., and Dougharty, N. A., *J. Catal.* **24**, 367 (1972).
22. Klimisch, R. L., Summers, J. C., and Schlatter, J. C., *in* "Catalysts for the Control of Automotive Pollutants" (J. E. McEvoy, Ed.); *Advan. Chem. Ser.* **143**, American Chemical Society, Washington, D.C., 1975, p. 103.
23. Williams, F. L., GM Research Laboratories, to be published.