

Effects of Platinum and Palladium Impregnation on the Performance and Durability of Automobile Exhaust Oxidizing Catalysts

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The performance and durability properties of noble metal-alumina oxidation catalysts are strongly influenced by the relative location of the metals along the radius of the porous catalyst pellets. Five Pt- and Pd-containing catalysts were prepared by systematically varying the noble-metal distribution along the radius of the catalyst pellets. The catalysts were poisoned on a dynamometer or sintered in a high-temperature furnace. The results showed sizable improvements in both steady-state and light-off performance when the catalyst had an outer shell of Pt and an inner shell of Pd.

INTRODUCTION

Since the fall of 1974, catalysts have been commercially employed to oxidize the carbon monoxide and hydrocarbon emissions from most automobiles sold in the United States. Although this application of catalytic technology has been remarkably successful in reducing automobile pollution, there is a continued interest in exploring ways of preparing catalysts having improved performance and durability characteristics.

The literature of catalyst poisoning in automobile exhaust has recently been reviewed by Shelef *et al.* (1), both for pellet-type and monolithic catalysts. This paper will deal only with pellet-type supported catalysts.

With the removal of lead from gasoline, the major cause of catalyst deactivation in current automobile systems appears to be from poisoning by trace quantities of phosphorus and lead in the fuel (2, 3) and the phosphorus in the engine oil (2, 4, 5). In addition to the effects of poisoning, the

"light-off" properties of the catalyst are also influenced by thermal sintering of the finely dispersed noble metals. Catalyst sintering in automobile applications has been recently discussed by Schlatter (6) and Dalla Betta *et al.* (7). This paper will deal with both catalyst poisoning and sintering.

As has been observed by, e.g., Klimisch *et al.* (8), the poisons penetrate the catalyst pellets in the form of more or less sharp waves. In subsequent work, Hegedus and Baron (9) successfully compared phosphorus poisoning experiments with the predictions of a mathematical model, demonstrating that the poison precursor (in this case, phosphorus) tends to penetrate the pellets with the rate of its diffusion in the pores. It was also found that the poisons are collected primarily by the micropores of the alumina support, leaving the macropores more or less intact and thus not altering the pellet's diffusive properties in a significant way (10). While exceptions to this type of poisoning have been found,

i.e., where the poisons actually plugged part of the macropores (11), in the typical case the poisons tend to deposit in a monolayer-like thickness over the support's surface (12) which explains why the pores are not usually plugged.

By considering the diffusive properties of the catalyst support, improved catalysts can be prepared (12, 13) which make use of the fact that both the poisoning reactions and the main reactions appear to be strongly influenced by diffusion at typical operating temperatures. The improvement is accomplished by properly designing the support's pore structure, (i.e., its diffusive properties), support surface area, and the impregnation depth of the noble metal employed.

Current pellet-type automobile catalysts employ both Pt and Pd, impregnated onto a porous alumina support. Experiments have shown that the catalytic performance and durability of these metals are different. In particular, Pt appears to be more resistant to poisoning than Pd [e.g., Ref. (12)], while Pd is more resistant to thermal sintering than Pt [e.g., Ref. (6)]. Palladium may also have a higher intrinsic chemical activity (14) for some reactions. Since one can impregnate the catalyst pellets in such

a way that the radial distribution of Pt or Pd is varied [e.g., Michalko (15), Roth (16), etc.], it was of interest to explore whether the differences in the catalytic poisoning and sintering behavior of Pt and Pd could be used to specify some optimum impregnation patterns so that catalysts with further improved performance and durability characteristics would result. This work will explore the possibilities given by the variation of catalyst impregnation profiles, for application in oxidative automobile catalytic converters. We will employ noble metal loadings similar to commercial levels, for both Pt and Pd.

EXPERIMENTAL

A. Catalyst preparation. To assess the importance of metal location in the pellets, five alumina-supported catalysts were prepared. The catalysts had the following configurations: Pt (exterior)/Pd (interior), designated Pt/Pd; Pd (exterior)/Pt (interior), designated Pd/Pt; coimpregnated Pt and Pd (both exterior), designated Pt-Pd; Pt (exterior), designated Pt; and Pd (exterior), designated Pd. These catalysts, together with some of their properties, are listed in Table 1.

TABLE 1
Properties of the Catalysts

Property	Pt/Pd	Pd/Pt	Pt-Pd	Pt	Pd
Pt band ^a					
Begins at (μm)	0	77 \pm 18	0	0	—
Width (μm)	82 \pm 36	To center	>100	82 \pm 36	—
Pd band ^a					
Begins at (μm)	107 \pm 16	0	0	—	0
Width (μm)	37 \pm 7	100 \pm 18	\sim 100	—	100 \pm 18
Pt (wt%)	0.036	0.038	0.040	0.036	—
Pd (wt%)	0.021	0.018	0.016	—	0.018
Metal dispersion (%) ^b					
Fresh catalysts	61	62	55	68	53
Sintered catalysts	10	15	8	3	39

^a Values given are the mean of 10 pellets \pm SD, determined by the SnCl_2 technique (15).

^b Effective dispersions, computed from CO chemisorption measurements by assuming 1:1 stoichiometry for both Pt and Pd atoms.

To prepare the Pt/Pd and the Pt catalysts, an aqueous solution of $\text{H}_2\text{PtBr}_6 \cdot 9\text{H}_2\text{O}$ (pH = 2.7) was impregnated on alumina. Due to its high reactivity with the alumina surface, H_2PtBr_6 was found to give particularly sharp, shallow metal penetrations. The catalyst was dried overnight and then calcined for 4 hr at 550°C. It was then divided into two parts. One half was retained and is designated as Pt. The other was impregnated with a PdCl_2 solution (at pH = 2.5), containing 4 wt% HF (0.182 ml of HF/ml of solution). The presence of HF causes the Pd to form a subsurface layer, apparently by blocking the alumina sites near the surface of the pellet, so that the Pd is forced deeper into the pellet before finding reactive alumina sites.

The coimpregnated [that is, Pt (exterior)/Pd (exterior)] catalyst was prepared by impregnating the alumina with an aqueous solution of chloroplatinic acid and PdCl_2 at a pH of 2.0. The resulting catalyst was dried overnight and then calcined for 4 hr at 550°C. Electron microprobe studies indicated that Pd tends to deposit closer to the exterior of the pellets than Pt if the above procedure is followed.

The preparation of the Pd/Pt and Pd catalysts first involved impregnating the alumina with a PdCl_2 (pH = 2.4) solution. At this pH a very sharp Pd profile was obtained at the outer surface of the catalyst pellets. After drying and calcination, the catalyst was divided into two portions. One was retained and designated as Pd while the other was impregnated with an aqueous solution containing H_2PtCl_6 and citric acid (0.00243 g of citric acid/ml of solution) at a pH of 2.3. Citric acid (15) appears to function similarly to HF by forcing the Pt into the interior of the alumina pellets. This treatment yielded a catalyst containing an inner core of Pt.

The alumina support used to prepare the catalysts was in the form of 0.32-cm-diameter spheres (surface area = 93 m²/g

and total pore volume = 0.723 cm³/g). The location of the noble metals, the noble-metal content, and the noble-metal dispersions of the five catalysts after preparation are given in Table 1.

The Pt and Pd loadings (weight percentage) were selected to stay similar from catalyst to catalyst. This, together with similar impregnation depths, was achieved within the experimental error of our preparations (Table 1).

B. Accelerated catalyst poisoning experiments. The catalysts were poisoned in a reactor which contained four screen trays in series, each approximately 250 cm³ in volume. By sampling and analyzing the catalyst on these trays, poison profiles along the reactor could be determined. The reactor was fed by the exhaust of a 5.7-liter V-8 engine. The engine operated at 1800 rpm on an engine dynamometer, at a manifold vacuum of about 47 kPa. The air-fuel ratio was 15.5 (an oxidizing exhaust). The fuel contained 0.023 g of Pb/liter, 0.117 g of S/liter, and 0.007 g of P/liter. In order to stabilize the poison emissions, the engine and exhaust system were equilibrated by operating on the poison-containing fuel for about 3 days before the first catalyst poisoning experiment.

The exhaust to the catalyst typically contained 0.29–0.34% CO, 1.16–1.20% O₂, and 280–320 ppm of hydrocarbons. The space velocity was about 115,000 hr⁻¹ (STP). During the experiments, the catalyst bed temperature was approximately 570°C. This accelerated poisoning experiment simulated about 400 hr of real-life exposure in about 40 hr. At the end of the test, samples of the catalysts were taken from the top of each of the four reactor trays for analysis.

C. Catalyst characterization. The noble-metal penetration depths in the alumina pellets were measured by boiling the pellets in an aqueous solution of SnCl_2 (15), and photographing the resulting darkened layers under a microscope. The depths of lead

and phosphorous penetrations into the poisoned catalysts were determined by electron microprobe. The noble-metal dispersions were determined by CO chemisorption.

Activity measurements were carried out both *in situ* during the accelerated durability test in the test cell and also in the laboratory. In the test cell we measured the hydrocarbon and carbon monoxide conversions at steady-state conditions [at 570°C and a space velocity of 115,000 hr⁻¹ (STP)]. In the laboratory reactor system, CO and propylene conversions were determined as a function of temperature. The laboratory reactor consisted of a 1.9-cm-i.d. stainless steel pipe which was heated by a tube furnace. An inert SiC packing served as the preheater. A catalyst charge of 10 cm³ [at a space velocity of 85,000 hr⁻¹ (STP)] was used. The laboratory feed stream consisted of 0.3% CO, 0.025% propylene, 1.5% O₂, 10% CO₂, and 10% H₂O in nitrogen. The programmed heating rate was 10°C/min.

RESULTS AND DISCUSSION

A. High-Temperature Performance

The conversions of hydrocarbons (Fig. 1) and carbon monoxide were observed as a

function of exposure time during the accelerated poisoning experiments on the dynamometer. The CO conversions are not shown here.

The first step in the experiment involved stabilizing the catalysts on an indolene-clear fuel for about 15 min in order to obtain a measure of their initial performance. Both the initial HC and CO conversions were dependent upon the noble-metal species and upon the relative location of the noble metals. For both hydrocarbons and carbon monoxide, the Pt/Pd configuration gave the best initial high-temperature performance while the others were about 10% lower.

While it is tempting to discuss the intrinsic differences in initial performance of the five catalysts, it cannot easily be done because of the complex interactions of the kinetic and diffusive effects at the temperature of the measurements. Thus, we will only discuss the overall difference in catalyst performance as determined by the combined diffusion-reaction process.

Exposure of the catalysts to the poison-containing exhaust (by switching to the poison-containing fuel) resulted in an almost instantaneous drop in their activity

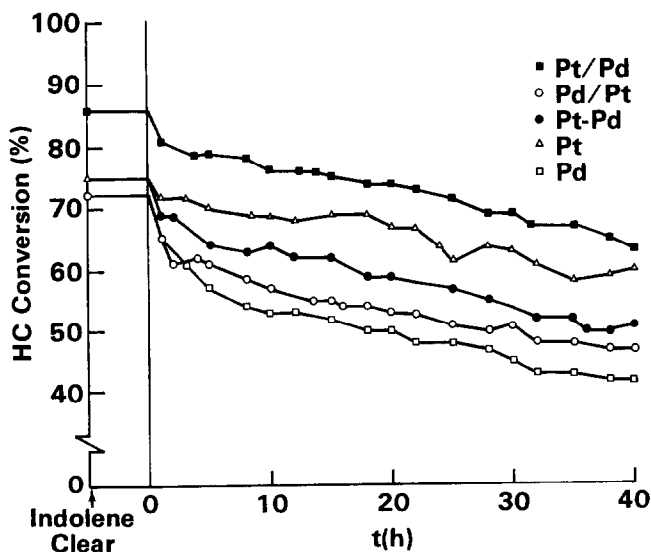


FIG. 1. Hydrocarbon conversions during the accelerated poisoning experiments.

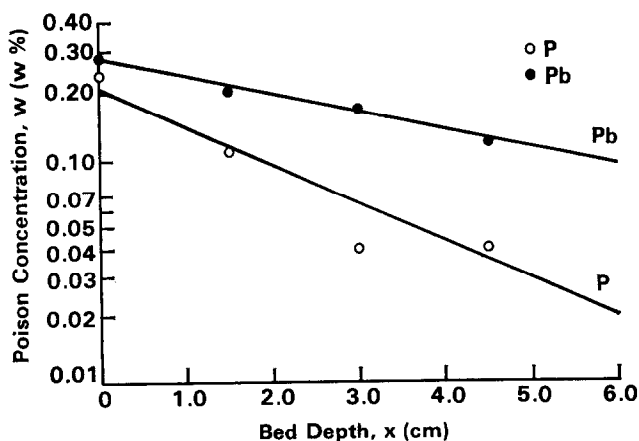


Fig. 2. Distribution of phosphorus and lead for Pt/Pd catalyst along the length of the catalyst bed.

as Fig. 1 demonstrates. Earlier work (17) has shown that this rapid (and reversible) drop in activity is largely associated with the halogen scavengers in the motor mix that was used as a source of Pb in the test fuel. The drop in activity ranged from 5 to 7% for the HC conversions and from 5 to 10% for the CO conversions, under the conditions of our experiments. The smallest drop was associated with Pt and the largest drop with Pd, for both HC and CO conversions, in agreement with previous observations (17, 18).

After the first hour of exposure to the exhaust of the poison-containing fuel, the performances of the five catalysts, in order of descending HC activity, are as follows (cf. Fig. 1): Pt/Pd, Pt, Pt-Pd, Pd/Pt, and Pd.

The Pt/Pd configuration gave the highest HC and CO conversions both on indolene-clear fuel and also on the fuel which contains halogens. This is highly significant since it means that both the HC and CO conversions were enhanced by the same type of noble-metal configuration.

As the catalysts were poisoned by P and Pb, the differences in their conversion performances became more pronounced. After 40 hr of exposure, the following order of HC activity was observed (Fig. 1): Pt/Pd, Pt, Pt-Pd, Pd/Pt, Pd.

Thus, we see that the Pt/Pd configuration, in addition to its best initial performance, is also superior for poison resistance. A similar sequence was observed for CO.

The catalyst configuration that contained Pd at the outer edge of the pellets experienced the strongest deactivation for both HC and CO oxidation. This observation is consistent with the fact that Pd is thought to be more susceptible to poisoning than Pt (8, 12), and that the poisons penetrate the catalyst pellets in a sharp, diffusion-limited front (8, 9, 11-13) which, of course, selectively poisons the outer shell of the catalyst pellets.

It is important to note the effect of having an inner band of Pd beneath the outer layer of Pt. The higher hydrocarbon activity of the Pt/Pd catalyst is undoubtedly the result of the oxidation in the interior of the catalyst pellets of HC species that are difficult to oxidize.

After the 40-hr poisoning experiments, samples were removed from all four trays of the sectioned catalyst bed and chemically analyzed for P and Pb. The contaminant penetrations were determined by electron microprobe. Figure 2 is typical of the poison distribution along the length of the catalyst bed: Both P and Pb are exponentially distributed along the bed for all five catalysts. The poison profiles were

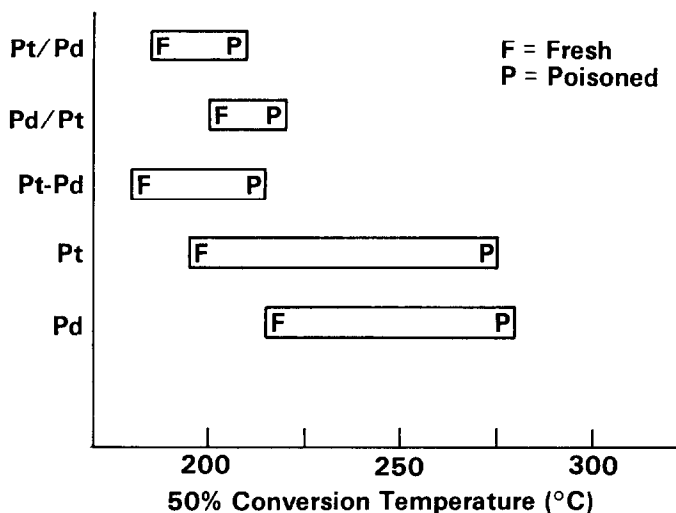


Fig. 3. Fifty percent conversion temperatures of CO for fresh and poisoned catalysts.

integrated along the bed by using the relationship,

$$\bar{w} = \frac{1}{L} \int_0^L w dx = \frac{e^b}{aL} (e^{aL} - 1),$$

where a is the slope and b is the intercept of the $\ln w - x$ linear regression [w is the poison concentration (weight percentage), x is the axial coordinate in the catalyst bed (centimeters), and L is the total depth of the catalyst bed (centimeters)].

The penetrations of P and Pb into the catalyst pellets were also exponentially distributed along the length of the catalyst bed. The integral average P penetrations ranged from 9 to 14 μm , and the integral average Pb penetrations ranged from 3 to 5 μm for the five catalysts. These findings indicate that both P and Pb followed the diffusion-limited shell progressive poisoning mechanism (9) in these steady state experiments. The data also indicated that P determines the leading edge of the Pb- and P-containing poison front in the catalyst pellets.

When comparing the poison penetration depths with the impregnation depths of the catalysts (Table 1), we found that the poisons penetrated only a small portion of

the outer shell of the pellets and that the metal located in the inner shell (Pd in the case of Pt/Pd, Pt in the case of Pd/Pt) remained unpoisoned.

B. Conversion-Temperature Behavior

A temperature-programmed laboratory reactor was used to generate conversion-inlet temperature curves for the fresh and poisoned catalysts. Figure 3 displays the temperatures required for 50% CO conversion. The 50% propylene conversion temperatures were also determined.

The laboratory reactor was filled with catalysts taken from the inlet tray of the test cell reactor, and thus the poison exposures of the catalysts in Fig. 3 correspond to the inlet poison levels (Fig. 2) and penetrations. Since these inlet poison levels are higher than the integral average poison exposures, the equivalent "age" of the catalyst samples used in the conversion-temperature experiments is more similar to an 80,000-km catalyst, as opposed to the integral averaged poison levels which resemble a 32,000-km catalyst.

During the course of the experiments, we observed that repeated conversion-temperature run-ups showed improved light-off

performance. That is, the catalyst lit off at a lower temperature in the second experiment than in the first. This difference was generally on the order of 5 to 30°C. We considered the first experiment as a pretreatment process and listed only the results of the second run-ups.

There is only a relatively small difference in the fresh light-off performance of the catalysts for both propylene and CO, with the exception of Pd. The sequence in order of increasing temperature required for 50% conversion is:

Propylene Pt/Pd, Pt-Pd, Pt, Pd/Pt,
and Pd
CO Pt-Pd, Pt/Pd, Pt, Pd/Pt,
and Pd.

These sequences are similar to those observed for high-temperature behavior (see Fig. 1 for HC). The catalysts with Pd near the outer edge of the pellets gave the poorest light-off performance. Noteworthy is the very poor light-off performance of the Pd catalyst which is significantly improved if Pt is added (Pd/Pt, Pt-Pd).

More interesting than the light-off activities of the fresh catalysts is the light-off performance after poisoning (Fig. 3). The

sequence of increasing temperature required for 50% conversion is as follows:

Propylene Pt/Pd, Pt-Pd, Pd/Pt, Pt,
and Pd
CO Pt/Pd, Pt-Pd, Pd/Pt, Pt,
and Pd.

The light-off temperatures increased by 20 to 90°C upon aging. The differences in light-off performance of the various poisoned catalyst configurations are very large, e.g., the light-off temperature of Pd for propylene is about 90°C higher than that of Pt/Pd. The Pt/Pd configuration exhibits the best performance, with the coimpregnated Pt-Pd catalyst being a close second. It is also interesting to note that the deterioration in light-off activity for propylene is somewhat greater than for CO, for all catalyst formulations.

C. Conversion Behavior of Sintered Catalysts

As expected, after the catalysts were sintered for 7 hr at 870°C in air, the Pt catalyst experienced the greatest loss in metal dispersion (from 68 to 3%), while the Pd catalyst lost the least (from 53 to 39%). The three Pt- and Pd-con-

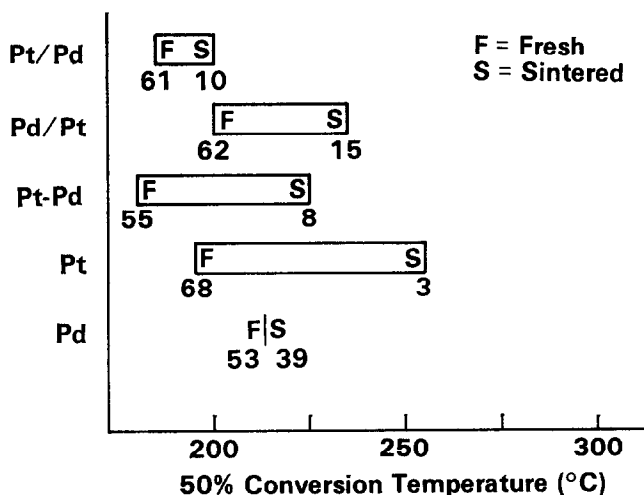


FIG. 4. Fifty percent conversion temperatures of CO for fresh and sintered catalysts. The numbers indicate dispersion (percentage).

taining catalysts had dispersions between 8 and 15% upon sintering.

The Pd catalyst experienced no deterioration in either propylene or CO light-off temperature upon sintering (Fig. 4). In contrast, the Pt catalyst suffered the greatest loss in light-off activity. After sintering, the Pt/Pd catalyst had the highest light-off activity for both propylene and CO. The coimpregnated Pt-Pd catalyst lost considerable light-off activity for both propylene and CO. The sequence of the catalyst preparations, in order of increasing temperature required for 50% conversion after sintering, is:

Propylene	Pt/Pd, Pt-Pd, Pd/Pt, Pd,
	and Pt
CO	Pt/Pd, Pt-Pd, Pd/Pt, Pd,
	and Pt.

Therefore, the best configuration to retain light-off activity after sintering is Pt/Pd, that is, Pt impregnated at the outer shell of the pellet and Pd in a separate band subsurface.

CONCLUSION

It has been shown that both the initial performance and the poisoning and sintering durability of oxidation catalysts are strongly influenced by the manner in which they are impregnated by a given amount of Pt and Pd. This was observed both for high-temperature, diffusion-influenced behavior of the catalysts and also for their light-off performance, and it holds for both HC and CO oxidation.

In particular, the results showed that improvements, in both steady-state and light-off performance, are possible if the catalyst pellets are impregnated by an outer shell of Pt and an inner shell of Pd. This configuration, then, appears to be the best use of a given amount of Pt and Pd in automobile exhaust oxidation catalysis, at least under the conditions covered by our experiments.

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