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# Interaction of Cerium Oxide with Noble Metals

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Ce oxide interacts with noble metals to affect greatly the metal dispersions and CO oxidation and three-way conversion activities. For fresh Pt catalysts the apparent metal dispersions decrease with increasing Ce content. For fresh Pd catalysts, on the other hand, the metal dispersions are independent of Ce loading. Thermal aging of $Pt/Ce \cdot Al_2O_3$ catalysts results in serious losses in apparent Pt dispersion. The apparent dispersion of the aged $Pt/Ce \cdot Al_2O_3$ catalysts depends on the gaseous environment (air or $H_2$) in which the catalysts are aged. Infrared spectroscopic investigations of CO chemisorption over Pt and $Pt/Ce \cdot Al_2O_3$ catalysts revealed that Ce promotes the oxidation of Pt. Ce did not affect CO chemisorption over the fresh $Pd/Ce \cdot Al_2O_3$ catalysts. To determine if bulk compound formation between the noble metals and Ce oxide could occur during thermal aging, mixtures of $Pt/CeO_2$ and $Pd/CeO_2$ were heated (600 and 900°C, 6 hr) in air and $H_2$. None were observed for the Pd system. However, at 900°C in $H_2$, Pt reacted to form $Pt_5Ce$. The $Pt_5Ce$ was identified by X-ray diffraction. Small quantities of Ce oxide (0.6–1.3 wt% Ce) enhance the oxidation of CO over fresh Pt and Pd catalysts. With increasing quantities of Ce the CO conversion activity of the fresh Pt catalysts greatly deteriorates while no such deterioration is observed for Pd. The effect of thermal aging on catalytic activity was studied under oxidizing (air), inert ($N_2$), and reducing ($H_2$) conditions. When aged in air, the activity of Ce-containing Pt and Rh catalysts greatly deteriorated. However, thermal aging in $H_2$ resulted in little or no activity loss under the conditions employed. The three-way activity of an air-aged Rh catalyst could be mostly regenerated upon high-temperature exposure to $H_2$.

## INTRODUCTION

Automobile emission control catalysts contain noble metals as the active components. In addition, base metals are added to many formulations in order either to improve performance or to stabilize the catalyst towards thermal aging effects.

Gandhi *et al.*, for example, claim that base metal oxides are effective for storing oxygen and are effective as water–gas shift components for three-way catalysts (*1*). Several patents have recently been issued that claim that rare earth oxides have beneficial effects during automotive catalytic processes. Wu has surveyed this work (*2*) and reports that rare earth oxides are referred to as promotors, activators, dispersers, stabilizers, and even as catalysts for NO control (*3–7*).

The bulk of published information on rare earth additives concerns primarily fresh catalytic performance and fresh catalyst characterization. Aging could drastically alter the properties of the fresh catalysts. Indeed, this has been shown to be the case for Pt/Rh/Ce three-way catalysts (*8*). Hegedus *et al.* have shown that Ce addition results in an enhancement of CO conversions for such three-way catalysts (*8*). However, upon thermal aging in ambient air, a deterioration in CO con-



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TABLE 1

Properties of the $Ce \cdot Al_2O_3$ Supports

| Ce (wt%) | Compound identity by XRD | Surface area ($m^2/g$) | Pore volume ($cm^3/g$) |
|---|---|---|---|
| 0 | $\gamma$-$Al_2O_3$ | 116 | 0.785 |
| 0.6 | $\gamma$-$Al_2O_3$ | 113 | — |
| 1.3 | $\gamma$-$Al_2O_3$ | 112 | 0.736 |
| 4.4 | $\gamma$-$Al_2O_3$, $CeO_2$ | 104 | 0.656 |
| 13.0 | $\gamma$-$Al_2O_3$, $CeO_2$ | 96 | 0.586 |

version results that is significantly more severe than is observed for their non-Ce-containing counterparts. This deterioration in CO conversion was attributed to an interaction between Ce and Pt. Pd appeared to resist CO activity deterioration upon thermal aging in air. The apparent interaction of Ce and Pt may be similar to that recently reported to exist between $TiO_2$ and noble metals (*9*).

The present study was conducted to probe the effects of Ce oxides on the properties of alumina-supported Pt, Pd, and Rh catalysts. Furthermore the role of gaseous environment in thermal aging was studied.

## EXPERIMENTAL

*Catalyst preparation.* $Ce(NO_3)_3$ solutions were impregnated onto porous $\gamma$-$Al_2O_3$ spheres (0.32-cm diameter, 120 $m^2/g$ surface area). These solutions were acidified with HCl (pH 1.12) in order to place the Ce uniformly along the pellet radius. The success of this operation was confirmed by electron microprobe measurements. Some of the properties of the $Ce \cdot Al_2O_3$ supports are given in Table 1. After calcining in air (500°C, 4 hr), the noble metals (Pt or Pd) were placed uniformly on supports which contained from 0 to 13.0 wt% Ce. This was accomplished by impregnating HCl solutions (pH 1.12) of either $H_2PtCl_6$ or $PdCl_2$ onto the supports, air drying, and then calcining the catalysts in air (500°C, 4 hr). The location of the Pt and Pd was determined by the $SnCl_2$ staining method (*10*). A list of the catalysts (laboratory catalysts) is given in Table 2. These catalysts were thermally aged (700–900°C) in either ambient air, $N_2$, or 5 vol% $H_2$ for 6 hr.

A series of Pt catalysts was prepared similarly on supports which contained from 0 to 8.5 wt% Zr. $ZrO(NO_3)_2$ was used as the source of Zr. These catalysts were thermally aged in air for 6 hr at 900°C.

A series of Pt and Rh catalysts was prepared for study in the test cell. They were prepared in a manner similar to the previously described catalysts except that the noble metal impregnating solutions were not acidified with HCl. Two levels of Ce were used: 0 and 1.3 wt%. After final calcination in ambient air (500°C, 4 hr), each catalyst batch was divided into three parts. One part was retained and designated as a fresh catalyst. One part was thermally aged in ambient air at 800°C for 4 hr, and

TABLE 2

Laboratory Catalysts

| Pt (wt%) | Pd (wt%) | Ce (wt%) | Aging conditions[a] |
|---|---|---|---|
| 0.050 | — | 0–13.0 | None |
| 0.050 | — | 0–13.0 | 900°C, 6 hr |
| 0.050 | — | 0, 1.3 | 700°C, 6 hr |
| 0.050 | — | 0, 1.3 | 800°C, 6 hr |
| — | 0.020 | 0–13.0 | None |
| — | 0.020 | 0–13.0 | 900°C, 6 hr |

[a] Heated in ambient air.

TABLE 3

Test Cell Catalysts

| Pt (wt%) | Rh (wt%) | Ce (wt%) | Aging conditions |
|---|---|---|---|
| 0.050 | — | 0, 1.3 | None |
| 0.050 | — | 0, 1.3 | 800°C, 4hr, air |
| 0.050 | — | 0, 1.3 | 800°C, 4 hr, $H_2$ |
| — | 0.002 | 0, 1.3 | None |
| — | 0.002 | 0, 1.3 | 800°C, 4 hr, air |
| — | 0.002 | 0, 1.3 | 800°C, 4 hr, $H_2$ |

one part was thermally aged in 5 vol% $H_2$ at 800°C for 4 hr. A list of these catalysts (test cell catalysts) is given in Table 3.

*Catalyst characterization.* Various methods of physical characterization were employed during the course of this study. Among these were noble metal dispersions determinations by the flow CO method (*11*). The CO uptake measurements were made by first heating the catalyst in $H_2$ for 1 hr at 500°C. The system was flushed with He at 500°C and was followed by the addition of $O_2$. The system was again flushed with He and cooled to room temperature in $H_2$. The CO uptakes were then determined for the clean reduced surfaces.

The chemisorption of CO on 1 wt% $M/Al_2O_3$, 13.0 wt% $Ce \cdot Al_2O_3$, and 1 wt% $M$/13.0 wt% $Ce \cdot Al_2O_3$ ($M$ = Pt, Pd) was studied by infrared spectroscopy. The experimental apparatus and the sample preparation techniques have been described previously by Chang and Hegedus (*12*). Equal quantities (0.07 g) of finely powdered unimpregnated alumina or 13 wt% $Ce \cdot Al_2O_3$ (for the reference disc) and $M/Al_2O_3$ or $M$/13.0 wt% $Ce \cdot Al_2O_3$ (for the sample disc) were pressed into circular, self-supporting discs of 20-mm diameter, at 6000 kg pressure. The adsorption of CO was investigated in a flow system at 250 and 350°C and in a static system at room temperature. Catalyst pretreatment consisted of heating the sample in $N_2$ for 30 min, followed by a 5 vol% $H_2$ treatment for 30 min, and finally a second $N_2$ treatment for 30 min. All the treatments were made at 400°C. Only the fresh catalysts were examined.

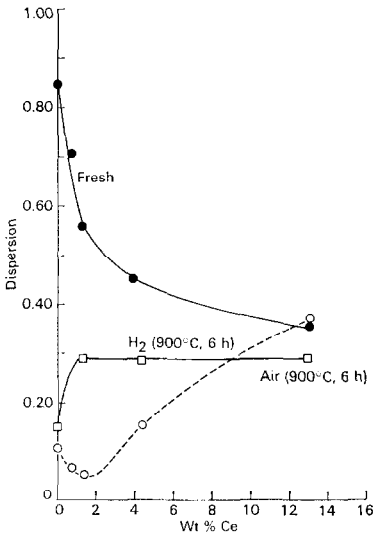


FIG. 1. Relationship of apparent Pt dispersion of fresh and thermally aged $Pt/Ce \cdot Al_2O_3$ catalysts with Ce loading.

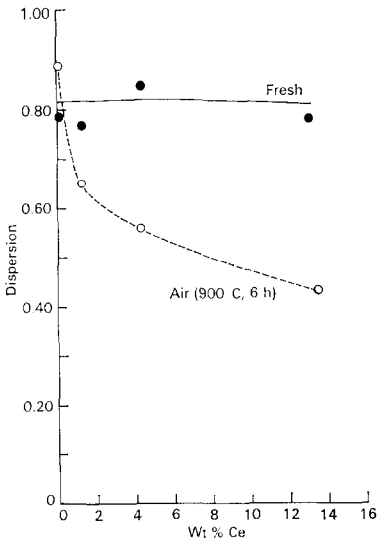


FIG. 2. Relationship of apparent Pd dispersion of fresh and thermally aged $Pd/Ce \cdot Al_2O_3$ catalysts with Ce loading.

In the laboratory CO conversions were measured as a function of temperature under strongly oxidizing conditions. A catalyst charge of 10 $cm^3$ [at a space velocity of 85,000 $hr^{-1}$ (STP)] was used. The reactor feedstream consisted of 0.3 vol% CO, 0.025 vol% propylene ($C_3H_6$), 1.5 vol% $O_2$, 10 vol% $CO_2$, and 10 vol% $H_2O$ in nitrogen. The programmed heating rate was 20°C/min.

Three-way conversions were determined on an engine dynamometer reactor system operated under steady-state conditions (*8*). The air/fuel ratio (A/F) was set to selected values (in the A/F range of 14.0 to 15.0), the system was stabilized, and the CO, NO,

TABLE 4

Calculated Apparent Particle Sizes of the Fresh and Air-Aged $Pt/Ce \cdot Al_2O_3$ Catalysts

| Ce (wt%) | Pt particle diameter (Å) | |
|---|---|---|
| | Fresh | Air aged |
| 0 | 11 | 89 |
| 0.6 | 13 | 130 |
| 1.3 | 16 | 170 |
| 4.4 | 22 | 63 |
| 13.0 | 28 | 27 |

and HC conversions were determined. A 1000-$cm^3$ converter which operated at a space velocity of $\sim$130,000 $hr^{-1}$ (STP) was employed. This very high space velocity was employed to accentuate the differences in conversion activity of the catalysts and for making these differences easier to observe. The inlet temperature of this converter was approximately 560°C.

## RESULTS

### *a. Characterization of the Supports*

Ce oxide is reported in the literature to react with $Al_2O_3$ to form a cerium–alumina compound (*13*). There was no direct evidence from this study of its formation or lack of formation. The X-ray diffraction data (Table 1) of the fresh and thermally aged (in air at 900°C for 6 hr) failed to shed light on the presence of cerium–alumina compound formation. $CeO_2$ was not detected in the low Ce loaded supports. This observation, of course, does not eliminate the possibility that $CeO_2$ was present in quantities too small to be detected by X-ray diffraction. Furthermore, the formation of a cerium–alumina surface species would not be detected by X-ray diffraction either.

Thermal aging in air at 900°C did not appear to alter the composition of the $Ce \cdot Al_2O_3$ supports. There was neither a change in the X-ray diffraction intensities of the $CeO_2$ bands nor the formation of new bands.

Surface area and pore volume data for the fresh $Ce \cdot Al_2O_3$ supports indicate that the addition of Ce oxide to $Al_2O_3$ by the incipient wetness method tends to plug some of the pores of this monomodal $Al_2O_3$ support with a concomitant loss of BET surface area. This small loss of surface area and decrease in pore volume are not expected to affect the conversion activity of the subsequently prepared uniformly impregnated catalysts for kinetically controlled reactions, such as the low-temperature oxidation of CO (*14*) or three-way reactions occurring near the stoichiometric point (*8*). The activity data presented subsequently appear to bear this out.

### *b. Interaction of Ce and Noble Metals*

Rare earth oxides have been described as being able to promote the dispersion of noble metals and to stabilize these dispersions from sintering (*5*). Thus, the effect of Ce loading on noble metal dispersions over fresh and thermally aged Pt and Pd catalysts was studied first.

The effects of Ce loading on apparent noble metal dispersions for the fresh and thermally aged Pt (air and $H_2$) and Pd (air) catalysts are shown in Figs. 1 and 2, respectively. The apparent dispersion of the fresh Pt catalysts decreased with increasing Ce loading but was independent of Ce loading for fresh Pd catalysts. Upon thermal aging in air, the apparent dispersion of the Pt-only catalyst decreased. At low Ce loadings, there was a further decrease. However, at higher Ce loadings ($\geq$4.4 wt%), the apparent dispersion increased. The apparent dispersion of the aged Pd catalysts decreased only moderately (*15*). Only negligible quantities of CO were adsorbed by either the fresh or thermally aged (900°C, 6 hr) samples of 13.0 wt% $Ce \cdot Al_2O_3$. In relation to the air aged $Pt/Ce \cdot Al_2O_3$ catalysts, aging in $H_2$ resulted

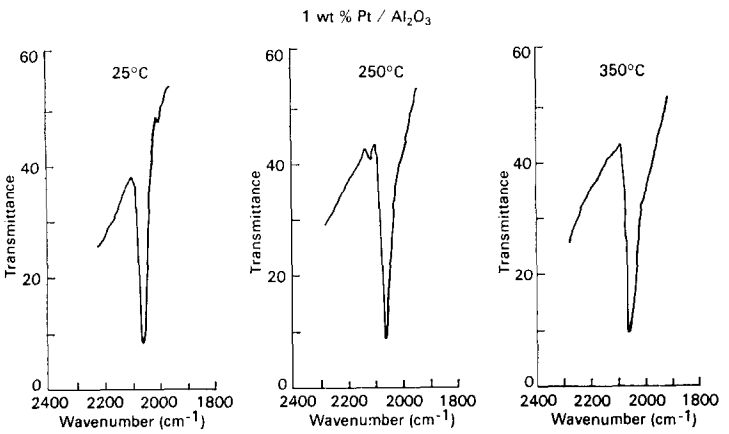


FIG. 3. CO adsorption on $Pt/Al_2O_3$.

in a relatively large increase in apparent Pt dispersion for the low Ce loaded catalysts (Fig. 1).

The apparent average Pt particle sizes of the fresh and air aged $Pt/Ce \cdot Al_2O_3$ catalysts were calculated from the relationship

$$d = 5\omega/\sigma A,$$

where $d$ is the particle diameter (Å), $\omega$ is the grams of noble metal per gram of catalyst, $\sigma$ is the metal density, and $A$ is the metal area per gram of catalyst (as obtained from the CO chemisorption measurements) (*16*). Table 4 lists the apparent average Pt particle sizes of the catalysts with Ce loading.

The fresh catalysts exhibit apparent average Pt particle diameters ranging from 11 to 28 Å as the Ce loading increases from 0 to 13.0 wt%. In the absence of Ce the apparent average particle size of the air-aged Pt catalyst was 89 Å. The apparent particle size increased to 170 Å as the Ce loading increased to 1.3 wt% and then declined to 27 Å at 13.0 wt% Ce.

To study the nature of the interaction of Ce with Pt and Pd, the chemisorption of CO on 1 wt% metal/$Al_2O_3$, 1 wt%

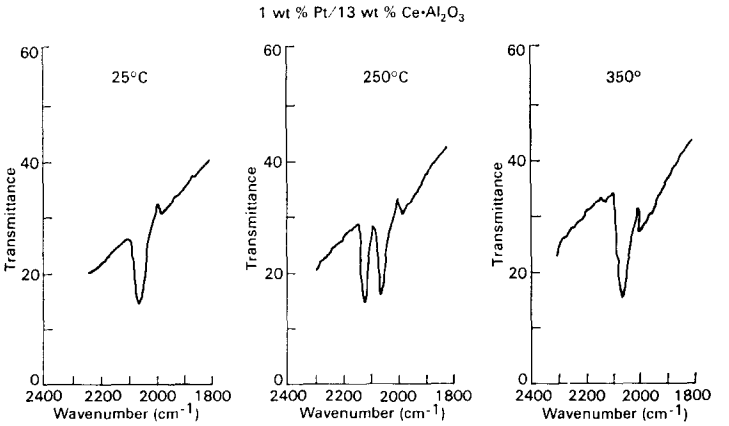


FIG. 4. CO adsorption on $Pt/Ce \cdot Al_2O_3$.

TABLE 5

Pt Dispersions and CO Conversion Data for the Fresh and Air-Aged $Pt/Zr \cdot Al_2O_3$ Catalysts[a]

| Zr (wt%) | Pt dispersions | | 30% CO conversion, temperature (°C) | |
|---|---|---|---|---|
| | Fresh | Aged | Fresh | Aged |
| 0 | 1.05 | 0.06 | 200 | 280 |
| 0.2 | 1.07 | 0.04 | 205 | 285 |
| 0.7 | 0.96 | 0.08 | 200 | 285 |
| 2.8 | 0.91 | 0.06 | 200 | 285 |
| 8.5 | 0.83 | 0.06 | 190 | 270 |

[a] Aging conditions: 6 hr in air at 900°C.

metal/13.0 wt% $Ce \cdot Al_2O_3$, and 13.0 wt% $Ce \cdot Al_2O_3$ was investigated by infrared spectroscopy. At room temperature a single adsorption band centered near 2080 $cm^{-1}$ was observed for the Pt catalysts (Figs. 3 and 4). None were observed for the 13.0 wt% $Ce \cdot Al_2O_3$ sample. The band intensity for the 1 wt% $Pt/Al_2O_3$ catalyst was significantly greater than that of the corresponding Ce-containing catalyst. This band is assigned to a linear stretching vibration of a single CO molecule chemisorbed on reduced Pt (*17*).

In the flow system at 250°C, a second band was observed for both Pt catalysts. It was centered at 2120 $cm^{-1}$. This band is assigned to CO chemisorbed on oxidized Pt ($Pt^{n+}$) (*18*). Increasing the temperature to 350°C had no significant effect on the intensity of the 2080 $cm^{-1}$ band for either Pt catalyst; however, the 2120 $cm^{-1}$ band virtually disappeared for both catalysts upon heating to 350°C.

The ir spectra of the fresh Pd catalysts revealed that CO chemisorption on Pd is independent of Ce loading. That is, the ir spectra for the 1.0 wt% $Pd/Al_2O_3$ and 1.0 wt% Pd/13.0 wt% $Ce \cdot Al_2O_3$ catalysts were virtually identical in terms of band location and band intensity. Adsorptions were observed at 1840 $cm^{-1}$ (bridged CO–Pd) and at 2080 $cm^{-1}$ (linear CO–Pd).

In order to see if bulk noble metal–Ce compounds could be formed during thermal aging, mixtures of $Pt/CeO_2$ and $Pd/CeO_2$ were heated for 6 hr at 600 and at 900°C in either air or 5 vol% $H_2$. None were detected by X-ray diffraction for the air-treated samples. In $H_2$ at 600°C none were observed. At 900°C in $H_2$, however, $Pt_5Ce$ was observed for the $Pt/CeO_2$ sample (*19*). No Pd–Ce species were detected by X-ray diffraction for any of the air or $H_2$ treatments.

As the data in Table 5 indicate, the Pt dispersions of neither the fresh nor the air-aged $Pt/Zr \cdot Al_2O_3$ catalysts are greatly affected by Zr.

### c. *Effect of Ce on Catalytic Conversions*

*CO oxidation.* Since Ce has been shown to have a profound effect on the CO adsorption properties of Pt catalysts, it was expected that this effect would be reflected in the CO oxidation conversion of the catalysts. Subsequently the CO conversions (as a function of temperature) of the $Pt/Ce \cdot Al_2O_3$ catalysts were determined in a laboratory integral reactor. The analogous Pd catalysts were also examined. The temperature required to oxidize 30% of the CO was taken as a measure of catalyst activity.

For the $Pt/Ce \cdot Al_2O_3$ catalysts the CO oxidation activity is a strong function of both Ce loading and thermal aging conditions of the catalysts (Fig. 5). At low Ce loadings (0.6–1.3 wt% Ce) the fresh $Pt/Ce \cdot Al_2O_3$ catalysts were more active (as evidenced by the lower temperatures required to oxidize 30% of the CO) than the Pt-only catalyst. This effect has been observed before for $Pt/Ce \cdot Al_2O_3$ catalysts (*20*). With increasing Ce loading ($\geq$4.4 wt%), the activity of the fresh $Pt/Ce \cdot Al_2O_3$ catalysts seriously deteriorated. Those catalysts thermally aged in $N_2$ exhibited CO oxidation activities intermediate to those aged in air and $H_2$.

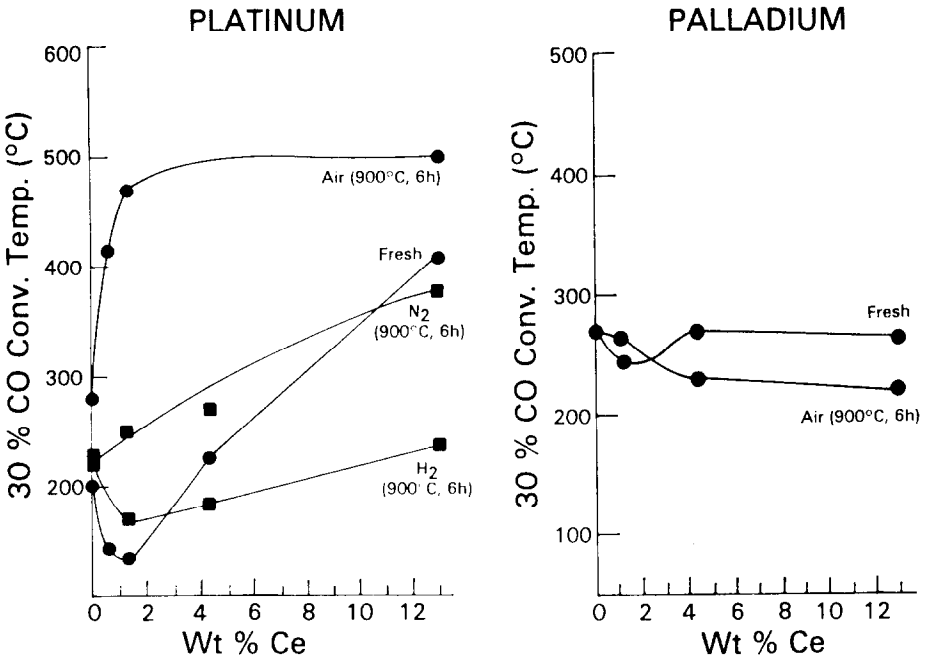


FIG. 5. Effect of Ce loading on the CO activity of fresh and thermally aged Pt and Pd catalysts.

An experiment was performed in an attempt to modify the activity of the fresh $Pt/Ce \cdot Al_2O_3$ catalysts. Samples of the fresh $Pt/Ce \cdot Al_2O_3$ catalysts (100 $cm^3$) were exposed to a stream of $SO_2(0.8\%)/O_2(4\%)$ in $N_2$ for 3 hr at 500°C. Since under these conditions $CeO_2$ reacts with $SO_2$ to reduce the $CeO_2$ (*21*), it was hoped that by treating the catalysts with $SO_2/O_2$ that the interaction between Pt and Ce could be destroyed and thus modify the CO conversion activity of the Pt. Michalko (*22*) has previously demonstrated the feasibility of such an approach by regenerating the activity of a Pb-poisoned $Pt/ZrO_2$ catalyst with $SO_2/O_2$. The $SO_2/O_2$ treatment presumably regenerated active Pt sites by precipitating the Pb from Pt as $PbSO_4$.

A comparison of Fig. 5 with Fig. 6 indicates that the treatment was successful. Both the enhancement of CO conversions at low Ce loading and the deterioration of CO conversions at high Ce loadings, for the most part, were affected by the $SO_2/O_2$ treatment. The $SO_2$-treated catalysts were only somewhat less active than the fresh non-Ce containing $Pt/Al_2O_3$ catalyst.

Since the effect of aging temperature was studied only at 900°C, it was decided to determine the temperature range in air for which Pt and Ce undergo significant interaction. Consequently, samples of the $Pt/Al_2O_3$ and the Pt/1.3 wt% $Ce \cdot Al_2O_3$ catalyst were also aged in air at 700 and 800°C. The Pt-only catalyst gradually declined in CO oxidation activity with increasing temperature (*15*) (Fig. 7). At temperatures up to 800°C the Pt/1.3 wt% $Ce \cdot Al_2O_3$ catalyst experienced only a relatively small loss in oxidation activity. At 900°C, as was seen previously, Pt appears to undergo extensive interaction with Ce oxide which results in serious activity deterioration.

Thermal aging experiments were also conducted with the $Pd/Ce \cdot Al_2O_3$ catalysts. These catalysts were thermally aged only in air (6 hr at 900°C). For the fresh Pd catalysts, a small enhancement in CO conversion with low Ce loadings was observed (Fig. 5). Compared to the analogous

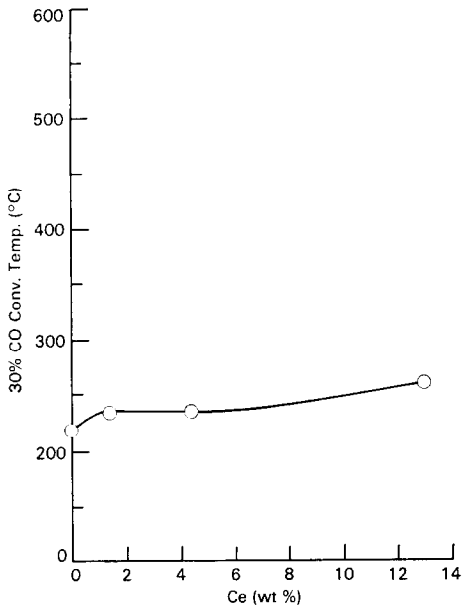


FIG. 6. Effect of $SO_2/O_2$ treatment on the CO conversion activity of fresh $Pt/Ce \cdot Al_2O_3$ catalysts.

Pt catalysts, the CO oxidation activity of the Pd catalysts was relatively insensitive to Ce loading. Upon thermal aging, the CO activity of the $Pd/Ce \cdot Al_2O_3$ catalysts actually improved.

As the data in Table 5 indicate, the CO conversions of neither the fresh nor the air-aged $Pt/Zr \cdot Al_2O_3$ catalysts are greatly affected by the Zr.

*Three-way conversion activity.* Next, an experiment was performed to determine the effect of thermal aging conditions on the three-way conversion activity of Pt, Rh, Pt/1.3 wt% $Ce \cdot Al_2O_3$, and Rh/1.3 wt% $Ce \cdot Al_2O_3$ catalysts. The thermal treatments involved exposure to either air or 5 vol% $H_2/N_2$ for 4 hr at 800°C.

Figure 8 shows the effect of thermal treatment on the NO and CO conversions of the Pt-only and Rh-only catalysts. The HC conversions are not shown here. The trends in HC conversions are very similar to those of CO. In the range of A/F examined (14.0–15.0) the fresh Pt-only catalysts are less active for both NO and CO (except at the highest A/F) conversion than the corresponding Rh-only catalysts (*23*). Furthermore, thermal aging in $H_2$ resulted in a conversion improvement for both Pt and Rh catalysts while thermal aging in air resulted in conversion activity deterioration for both Pt and Rh catalysts. Deterioration, however, was more severe for the Pt catalysts than for the Rh catalysts. When Rh is oxidized in air at temperatures above 700°C, it apparently interacts with $Al_2O_3$ to form an inactive species (*24*). High-temperature exposure to $H_2$ presumably regenerates active Rh sites. As shown previously (*23*) the low activity of Pt relative to Rh is due in part to $SO_2$ poisoning of less poison-resistant Pt.

Figure 9 shows the effect of thermal treatment on the NO and CO conversions over the Ce-containing Pt and Rh catalysts. In comparing the three-way conversions of the Pt and $Pt/Ce \cdot Al_2O_3$ catalysts it is apparent that 1.0 wt% Ce severely inhibits the activity of the fresh and air-aged catalysts (cf. Figs. 8 and 9).

For the Rh catalysts the effect of Ce on three-way activity is not as great as that observed for Pt catalysts. Furthermore, the activities of the two Rh catalysts aged in $H_2$ were virtually identical.

The extent of reversibility of the effect of thermal treatment on Rh catalysts was assessed in two experiments. The $H_2$ aged $Rh/Ce \cdot Al_2O_3$ catalyst was heated at 800°C in air for 4 hr followed by an activity measurement. This catalyst experienced a sharp decline in conversion (Fig. 9). Upon heating this same catalyst at 800°C in $H_2$ for 4 hr, much of the activity could be restored.

## DISCUSSION

Tauster and Fung have shown that under high-temperature reducing ($H_2$) conditions Ir can interact with a number of transition metal oxides such that almost no $H_2$ chemisorbs on the Ir (*25*). Although they did not study $CeO_2$, they did examine $ZrO_2$. As was found in this study, they

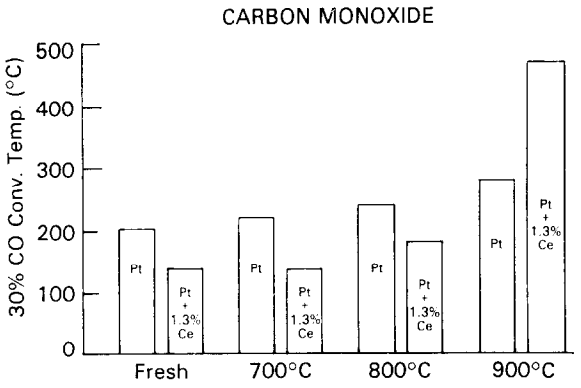


FIG. 7. Thermal aging of Pt and Pt/Ce catalysts: oxidation activity.

found no evidence that $ZrO_2$ interacted with the Ir.

It is apparent from this study that unlike $ZrO_2$, Ce oxide strongly interacts with noble metals. Furthermore, the interaction is a function of noble metal type and aging history. This can be clearly seen from the dispersion data contained in Figs. 1 and 2.

For the fresh $Pt/Ce \cdot Al_2O_3$ catalysts the apparent Pt dispersion decreases with increasing Ce content. These data indicate that the dispersion of Pt is relatively unstable in the presence of Ce oxide. The dispersion of Pd, by way of contrast, is virtually unaffected by Ce oxide for the fresh catalysts.

Is the loss of apparent Pt dispersion with increasing Ce loading due to agglomeration of the Pt during catalyst preparation or is it due to an interaction of the Pt and Ce which inhibits CO chemisorption? From the data generated during this study, it is difficult to answer this question unambiguously. The fact that the apparent dispersion data (Fig. 1) fail to correlate with the CO oxidation data (Fig. 5) does not necessarily mean that appreciable agglomeration does not occur during catalyst preparation. As was seen from both the ir spectra of the Pt-only and Pt/13.0 wt% $Ce \cdot Al_2O_3$ catalysts and the CO oxidation data, Ce oxide does interact with

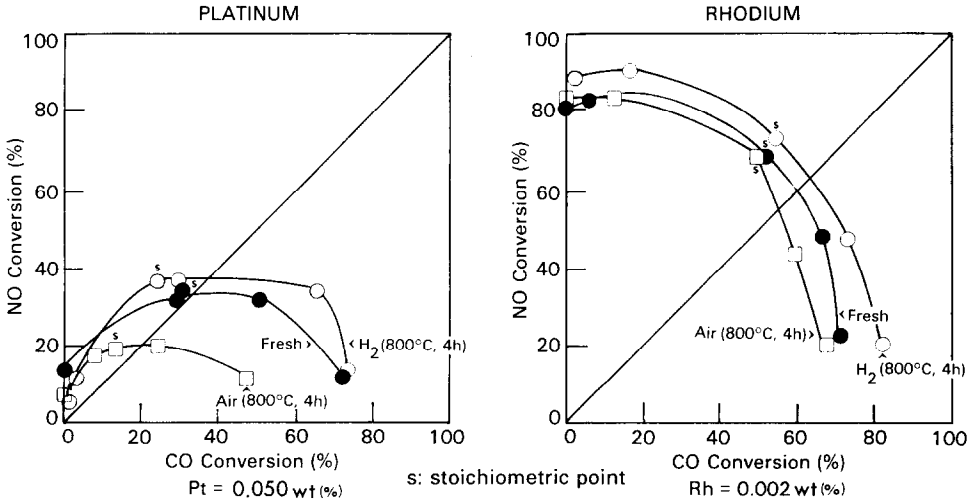


FIG. 8. Effect of thermal aging on the three-way performance of Pt and Rh catalysts.

the Pt. However, the dispersion data for the fresh $Pt/Ce \cdot Al_2O_3$ catalysts may well be an accurate reflection of Pt particle size.

If agglomeration does occur during catalyst preparation, it would appear, because of the relatively low temperature of calcination (500°C), that surface diffusional processes would be responsible (*26*). Two factors primarily control surface diffusion rates: the surface energy of the support and the interaction of the noble metal with the surface (*26*). As discussed previously, the support surface structure may undergo profound changes with increasing Ce loading. Since the effect of increasing Ce loading on the $Al_2O_3$ surface structure is not known, it is not possible to determine how the increase in Ce loading will affect the interaction of the noble metal with the support. Furthermore, the situation is complicated by the fact that the extent of Pt–oxygen bonding of the Pt and the support is a strong function of Pt dispersion. Katzer and Sayers have shown that when Pt is highly dispersed ($D \approx 1.0$) on $Al_2O_3$, the Pt is electron deficient, i.e., oxidized. At larger particle sizes (~20 Å) the Pt is present primarily as the bulk metal (*27*). In the presence of a powerful oxidizing agent such as $CeO_2$, it is conceivable that even relatively large particles of Pt ($\geq$20 Å) might be oxidized. Pd presumably exists as PdO under the conditions in which the experiments of this study were conducted (*28*).

In view of the difficulty of characterizing both the support surface and the state of the noble metal, it is difficult to rationalize why the dispersion of Pt decreases with increasing Ce loading but the dispersion of Pd does not.

The effect of Ce oxide on the surface chemistry of Pt and Pd was probed by studying CO chemisorption over the fresh Ce-free and Ce-containing Pt and Pd catalysts by infrared spectroscopy. The room temperature spectra of both the $Pt/Al_2O_3$ and Pt/13.0 wt% $Ce \cdot Al_2O_3$ catalysts reveal the presence of a single CO adsorption band centered at 2080 $cm^{-1}$ (Figs. 3 and 4). The band intensity for the $Pt/Al_2O_3$ catalyst is significantly greater than the band intensity of the Ce-containing catalyst. This observation is consistent with previous findings, namely, Ce oxide apparently destabilizes Pt with respect to sintering.

At 250°C a small band appears at 2120 $cm^{-1}$ in the spectrum of the $Pt/Al_2O_3$ catalyst (Fig. 3). For the Ce-containing catalyst

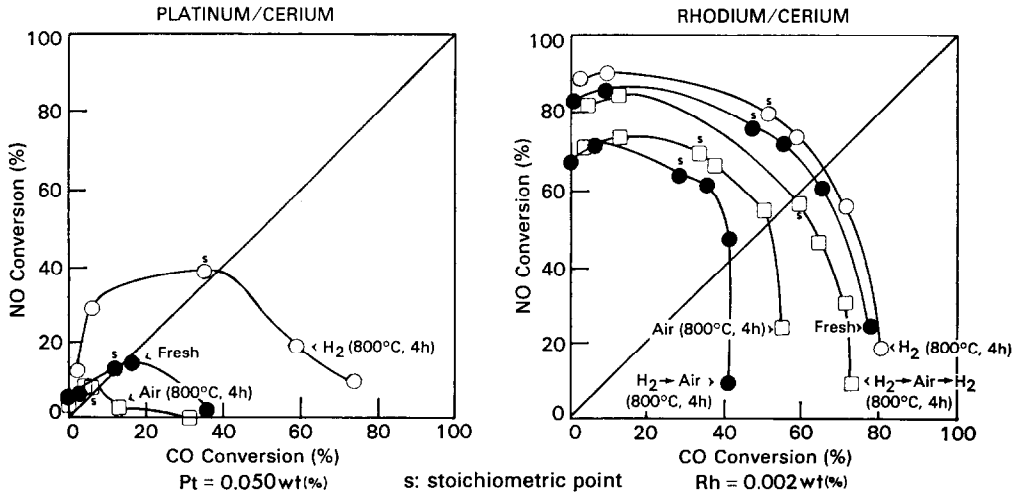


FIG. 9. Effect of thermal aging on the three-way performance of Pt and Rh catalysts.

the 2120 $cm^{-1}$ band which appears in the spectrum is much more intense (Fig. 4). This band which is assigned to CO chemisorbed on oxidized Pt sites presumably arises from trace amounts of $O_2$ in the ir cell. The origin of the intense 2120 $cm^{-1}$ band in the spectrum of the Ce-containing catalyst is very interesting. Ce is present as $CeO_2$ (identified by X-ray diffraction), and, since $CeO_2$ is a powerful oxidizing agent, it appears that it oxidizes some of the surface Pt sites. The absence of the 2120 $cm^{-1}$ band in the spectra of both Pt catalysts at 350°C suggests that at this temperature the CO in the flow system is able to reduce the oxidized Pt back to the metallic state, while 250°C is presumably not high enough.

On the basis of the data at hand, it is difficult to determine with certainty the effect that oxidized Pt sites have on CO oxidation for the $Pt/Ce \cdot Al_2O_3$ catalysts. Oxidized Pt is thought, however, to be less active for CO oxidation than reduced or metallic Pt (*18*).

In considering the CO oxidation data of Fig. 5, two points of interest emerge: the enhancement of CO conversion that occurs at lower Ce loadings (<2.0 wt%) and the deterioration of CO conversion that occurs at higher Ce loadings (>2.0 wt%). A similar CO activity pattern has been previously observed for $Th \cdot Al_2O_3$ catalysts with increasing Ce loadings (*29*).

Both activity phenomena must be due to Pt–Ce interactions since $Ce \cdot Al_2O_3$ by itself does not oxidize CO under the conditions that the activity measurements were made. Indeed the $SO_2$ poisoning experiment clearly demonstrates this. $SO_2$, a strong reducing agent, reacts with $CeO_2$, a strong oxidizing agent, to destroy the interaction of Ce oxide with Pt. This being the case, the CO conversion activity of the $SO_2$-poisoned $Pt/Ce \cdot Al_2O_3$ catalysts is essentially independent of Ce loading.

The presence of Ce oxide does not appear to affect the surface chemistry of Pd. The ir spectra for the two fresh Pd catalysts were virtually identical and this observation correlates well with the chemisorption data.

Thermal aging of the $Pt/Ce \cdot Al_2O_3$ catalysts drastically affects their apparent Pt dispersions. The dispersion data for the air-aged (900°C, 6 hr) $Pt/Ce \cdot Al_2O_3$ catalysts are difficult to rationalize. With increasing Ce loading, the apparent Pt dispersions first decrease and then increase. The decrease in dispersion can be rationalized easily enough, but the increase in dispersion is difficult to explain. Although similarly aged $Ce \cdot Al_2O_3$ was shown to adsorb only negligible quantities of CO at room temperature, it may be that when Pt is thermally aged in air and in the presence of large quantities of Ce oxide, the product resulting from a Pt–Ce interaction adsorbs more than one molecule of CO per Pt site. The calculated average Pt particle sizes of the air-aged $Pt/Ce \cdot Al_2O_3$ catalysts are clearly unreasonable (Table 4).

For the $H_2$-aged catalysts the Pt dispersions (except for the highest Ce loading) are significantly larger than those for the air-aged catalysts. This apparent enhancement in Pt dispersion may possibly be related to the formation of $Pt_5Ce$. Since $Pt_5Ce$ readily forms by heating Pt black and $CeO_2$ together (900°C, 6 hr), it seems likely that $Pt_5Ce$ would form on the supported $Pt/Ce \cdot Al_2O_3$ catalysts as well.

For Pt catalysts Dautzenberg and coworkers have observed that while thermal aging in $O_2$ results in significant sintering, thermal aging in $H_2$ does not (*30*, *31*). These authors present evidence that indicate that Pt–Al alloys form upon aging in $H_2$ at 675°C. The original Pt sites are regenerated upon exposing these alloys to $O_2$ at 400°C. Our findings appear qualitatively similar to those of Dautzenberg in that similar chemisorption trends are also observed for the air- and $H_2$-aged $Pt/Ce \cdot Al_2O_3$ catalysts.

Chemisorption data are generally useful for predicting the catalytic activity of kinetically controlled reactions [e.g., the low-temperature oxidation of CO (*14*)]. The implicit assumption of such predictions is that the site activity is unchanged by thermal aging. Clearly this is not the case for the $Pt/Ce \cdot Al_2O_3$ catalysts (cf. Figs. 1 and 4) and is true for the fresh $Pd/Ce \cdot Al_2O_3$ but not the air-aged $Pd/Ce \cdot Al_2O_3$ catalysts (cf. Figs. 2 and 4). In view of the complexity of the Pt–Ce chemistry (i.e., Ce's ability to oxidize Pt and to form alloys with Pt of the type $Pt_5Ce$), this lack of correlation between CO chemisorption and CO oxidation data should not be surprising. It is quite apparent that Pt site activity is a function of a number of parameters. Among these parameters are Ce loading (Fig. 1), gaseous aging environment (Fig. 1), and aging temperature (Fig. 6).

Both Pt and Rh exhibit pronounced changes in three-way conversions in the presence of Ce oxide. For $Rh/Ce \cdot Al_2O_3$ the harmful effects of air aging on three-way conversions can, for the most part, be reversed by a subsequent aging treatment in $H_2$. Thus, the nature of Rh–Ce interactions is dictated by the gaseous environment in which the catalyst is aged. Figures 8 and 9 indicate that the three-way conversions over $Pt/Ce \cdot Al_2O_3$ are strongly deteriorated upon aging.

## CONCLUSIONS

This study has shown that Ce oxide interacts with $Al_2O_3$-supported noble metals in a manner which affects both their dispersions and catalytic activity. The nature of the interaction is a function of the particular noble metal, aging temperature, and gaseous environment. The interactions are, in part at least, reversible as can be seen in the effects of $SO_2$ on the CO conversion of $Pt/Ce \cdot Al_2O_3$ catalysts and $H_2$ on the three-way conversions of $Rh/Ce \cdot Al_2O_3$.

This study has also raised some questions that must be answered by future work. For example: why do the Pt dispersions of air-aged $Pt/Ce \cdot Al_2O_3$ increase with high Ce loadings, what is the nature of the Pt–Ce interaction that occurs upon aging in air at 900°C, and finally what is the nature of the Pt–Ce interaction that results in an enhancement of CO conversion at relatively low Ce loadings for fresh $Pt/Ce \cdot Al_2O_3$ catalysts?

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