IMPACT OF SULFUR ON THREE-WAY CATALYSTS: COMPARISON OF COMMERCIALLY PRODUCED Pd AND Pt-Rh MONOLITHS

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ABSTRACT

Commercially-prepared Pt-Rh and Pd monolith catalysts were thermally aged then characterized for catalytic performance using a laboratory reactor to evaluate the magnitude and reversibility of the impact of sulfur on three-way activity. The SO_2 concentration in the feedstream was varied from 0 ppm to 30 ppm, which was comparable to sulfur levels in gasoline ranging from 0 to 450 ppm. Tests were first conducted using propylene and repeated using propane to represent the hydrocarbon mixture in exhaust.

Of the two catalysts, Pd showed better propylene lightoff activity while Pt-Rh showed better propane lightoff activity, regardless of the sulfur content. For each catalyst, increasing the sulfur concentration from 0 ppm SO_2 to 30 ppm SO_2 of sulfur resulted in a lightoff temperature increase by 40 to 60°C. Under warmed-up conditions, the loss of activity for HC, CO and NOx due to the presence of sulfur was greater under slightly rich conditions than under lean conditions for both Pd and Pt-Rh, while the magnitude of the impact on NOx and particularly on HC activity under warmed-up stoichiometric conditions was significant and much greater for Pd than for Pt-Rh catalyst. Using propylene, the effect of SO_2 on the activity of the Pd catalyst was partly reversible, while the effect on Pt-Rh was completely reversible. Using propane, the effect of sulfur on the activity of both catalysts was larger than for propylene. The resulting decrease in activity due to the presence of sulfur was partly reversible on Pt-Rh, but the poisoning of the Pd catalyst was mostly irreversible. Part of the irreversible poisoning effect is attributed to a direct interaction or reaction between SO_2 and Pd, while the other part is attributed to the promotional effect of SO_2 in hydrocarbon coking of the catalyst when alkane hydrocarbons are present.

1. INTRODUCTION

Organo-sulfur compounds are commonly present in nearly all commercially produced gasoline blends which are intended for vehicle use. These compounds are involved in the combustion process in the engine and are converted mainly into sulfur dioxide before entering the catalytic converter or converters. This form of sulfur has been demonstrated to deactivate vehicle exhaust catalysts. Prior work performed in the 1970's focused on the impact of sulfur on Pt and/or Pd supported on alumina catalysts operating under net oxidizing, or "lean" conditions [1-3]. Currently used three-way catalyst systems are far more complicated in that their washcoat formulations contain in addition to Pt, Rh, and sometimes Pd noble metals, a number of base metal oxides of Ce, La, Ni, Ba, Fe, Nd, and others. The exhaust adds to the complexity by cycling rapidly between net reducing and net oxidizing conditions when the vehicle operates under closed loop control. The cycling between these conditions may not be balanced under certain operating conditions such as a quick acceleration or deceleration or when a load condition is imposed. Moreover, the vehicle calibration may be slightly biased toward net lean or net rich operation. All of these conditions influence how SO_2 in exhaust interacts with the support, base metal oxides, and noble metal components in the catalyst and, in turn, affects activity.

Laboratory studies of the effect of sulfur on three-way activity showed that activity was inhibited particularly under rich conditions and mostly for catalysts containing both Pt and Pd, but activity was not significantly affected when the feedstream was cycled about a net stoichiometric point [4-6]. Sulfur has been demonstrated to poison the water-gas shift reaction and steam reforming reactions, [6-7] which is more important during operation under net stoichiometric or rich conditions since the availability of oxygen under these conditions is limited (HC and CO are easily removed by simple oxidation under lean conditions). It is also known from surface science studies that SO_2 dissociates on Pt, Rh, and Pd, forming adsorbed oxygen and adsorbed sulfur, the latter being difficult to remove in rich conditions [8-13]. Small coverages of elemental sulfur can significantly poison the noble metal surface for the adsorption of adsorbates such as CO [13]. Vehicle studies indicated that sulfur deteriorates the performance of three-way catalysts [14], and the magnitude of the impact was found to be calibration-dependent [5,15].

When three-way catalyst formulations began incorporating larger amounts of Ce (up to ~30 wt.% Ce) to provide a number of beneficial effects, including the enhancement of the A/F "window" in which three-way activity occurs, H_2S emissions in the exhaust became noticeable. These events prompted a number of studies of the mechanism of H_2S formation in three-way catalysts to suggest

methods of inhibiting the release of sulfur as H_2S in large "pulses". These studies showed that sulfur stored by the catalyst under net lean conditions was released under rich conditions [16]. Storage in lean conditions involves absorption and even reaction with the support and/or base metal oxide to form sulfates and sulfites [17,18]. Some of these species are strongly bound to the support and may be formed by the noble metal catalyzed oxidation of SO_2 to form SO_3^{-2} [9,10]. Previous studies have also shown that the uptake of SO_2 on CeO_2 is far greater than on Al_2O_3, further pointing to the role of CeO_2 in the storage of sulfur [16,19]. In reducing conditions, removal of sulfur occurs and involves reduction to H_2S, elemental sulfur, and reaction with CO to form COS. In Pt-Rh catalysts, the storage and removal of sulfur can be at least partially inhibited by a variety of methods, including the processing of the catalyst to reduce the amount of sulfur stored by the base metal oxide components, or adding a scavenging agent such as Ni or Cu [19-23].

The study of the impact of sulfur on three-way systems has recently gained interest again, as attention has turned to the reformulation of gasoline to reduce vehicle emissions as called for by the Clean Air Act amendments of 1990 and new regulations imposed by the state of California. One of the issues taken up by the Auto-Oil Industry Air Quality Study has been the effect of fuel sulfur on FTP converter efficiency in two vehicle fleets, one comprised of vehicles manufactured between 1979 and 1986, the other of vehicles manufactured in 1989. Both fleets showed a significant improvement in emissions when the sulfur content in fuel was reduced, leading to a recommendation that gasoline reformulation should include a reduction of sulfur level [15,24]. These and other vehicle studies also showed that the effects of sulfur are generally reversible when the fuel was changed from a relatively high sulfur content to a low sulfur content [25]. Ultimately, vehicle studies such as these are needed to better determine the effect of various sulfur content fuels and operating conditions on catalyst performance, but laboratory studies can provide a better understanding of sulfur storage, release and poisoning mechanisms and effects under well-controlled conditions to help in the design of these vehicle tests. Such studies have been carried out in our laboratory using newer technology three-way catalyst systems employing Pt and Rh [13, 26].

Recent attention has been placed on the use of Pd-based catalyst formulations because of their ability to catalyze the oxidation of hydrocarbons and CO at relatively low temperatures as a strategy to improve cold-start emissions and thus comply with low emission vehicle regulations, and because of the lower cost of Pd metal relative to Pt and especially Rh [27-32]. Three-way catalysts using Pd or Pd and Pt were evaluated in the late 1970's and early 1980's, but were found to be easily poisoned by sulfur [33,34]. Indeed, recent studies

conducted in this laboratory have confirmed Pd-containing catalysts were particularly susceptible to irreversible sulfur poisoning under isothermal exhaust-like conditions when compared to similar catalysts consisting of Pt and Rh supported on alumina [26, 36].

Recent developments in Pd catalyst technology have been demonstrated to improve the durability of the low temperature lightoff properties of this catalyst after repeated exposure to relatively high temperature exhaust [30,32,35]. Thus, these new catalyst formulations show promise for application as a close-coupled catalyst which can reach HC lightoff rapidly after cold-start. These new formulations may also be more resistant to sulfur poisoning.

The effect of SO_2 on these Pd catalyst formulations, however, has not been widely discussed in the published literature; thus the present study was performed to gain a better understanding of how sulfur affects the performance of a current production Pd catalyst intended for use in high temperature (up to 1000°C) conditions such as a close-coupled converter, and how the impact of sulfur compares to a current technology Pt-Rh three-way converter having a similar noble metal loading. Changes in lightoff and isothermal performances were measured as a function of increasing SO_2 concentration in a simulated exhaust feedstream using a laboratory reactor. Tests were first conducted using propylene as a model of the hydrocarbon species in exhaust, and then repeated using propane in a similar function. Additionally, the effect of sulfur on the performance of the catalysts during an air/fuel ratio scan was also evaluated.

2.EXPERIMENTAL ASPECTS

2.1 Catalysts

Two catalyst formulations were used in this study. The first, a Pd catalyst having a loading of 50 g/ft.^{3} (0.29 wt.%), was obtained in monolith form (cell density 400 cells/in^3). This washcoat formulation is considered to represent a state-of-the-art Pd catalyst for use in a rapid HC lightoff close-coupled (within 10-15" of the exhaust manifold) converter, and has been processed with several additives which serve to promote the activity of the Pd and to thermally stabilize the support and supported metal. The Pt-Rh monolith catalyst was also obtained in monolith form, having a cell density of 400 cells/in^3 and a loading of 23.5 g/ft^3 Pt, 1.68 g/ft^3 Rh (0.13 wt.% Pt, 0.0093 wt.% Rh). This washcoat is designed for use in converters which will be exposed to exhaust temperatures consistent with an underfloor location (at least 25-30" from the exhaust manifold), which are significantly lower than those encountered in a close-coupled location.

2.2 Thermal Aging Treatment

All of the catalysts were evaluated following a thermal aging treatment. The thermal aging was performed by placing the sample in the center of a tube furnace and downstream from a heat exchange zone. In this apparatus, the catalyst is heated mainly by the treatment gases which pass through a heat exchanger. Constant treatment temperature was maintained at a constant value using a thermocouple contacting the catalyst bed to control the furnace. The aging treatment consisted of alternating the gas feed between 5% O_2/N_2 and 5% H_2/N_2 at a rate of 0.1 Hz while maintaining the temperature of the catalyst at 1000°C for 4 h.

2.3 Activity Measurements

Both Pd and Pt-Rh catalyst formulations were evaluated for lightoff and isothermal activity using a laboratory reactor [37]. The composition of the feedstream was chosen to simulate vehicle exhaust, and the composition was controlled using a computer which has been interfaced with a bank of mass flow controllers. In the first series of tests, propylene was chosen to represent the alkene hydrocarbon species in the emissions as it is one of the most abundant hydrocarbon species in exhaust [38] and it figures significantly in the determination of total NMOG emissions since its reactivity factor is relatively high. The tests were repeated using propane to represent the alkane hydrocarbon mass emissions as the alkanes are believed to be among the most difficult of all hydrocarbons in vehicle exhaust to oxidize catalytically. The reactor is configured with a computer-controlled switching valve which alternates between a net reducing feedstream composition and an oxidizing feedstream composition so that the dynamic characteristics of exhaust produced by a vehicle operating under closed-loop control are simulated [37].

For lightoff testing, a sample was first prepared by cutting a section of the monolith having a facial dimension of 10 x 10 cells and a length of 1", was then thermally aged, then loaded into the reactor and stabilized in a nitrogen flow for 1 h at 100°C, and finally exposed to the simulated exhaust at 9 l/min while the temperature was decreased from 600°C to 100°C at 20°C/min. Evaluations were performed using a feedstream which cycled about the stoichiometric point at A/F =14.1 with an amplitude of ±0.5 A/F and a cycling frequency of 0.5 Hz. The sulfur level was held at a constant level during each lightoff test, but was changed between tests to determine the effect of sulfur on lightoff. The gas composition used for the lightoff tests is listed in Table 1.

Isothermal tests were performed using the same samples, which were stabilized in a nitrogen flow for 1 h at 500°C prior to exposure to the simulated exhaust feed. During the isothermal test, the sulfur concentration was step-

changed from 0 ppm to a predetermined level for 15 min, then step-changed to 0 ppm for an additional 30 min to determine the effect of sulfur on warmed-up activity and to determine the reversibility of the effect.

Table 1. Laboratory Reactor Simulated Exhaust, Cycled about Stoichiometry (Lightoff and Isothermal Tests)

Gas Component	Concentration
O_2	0.6 % (net)[1]
propylene (or propane)	300 ppm
CO	0.77 %
NO	500 ppm
H_2	0.2%
H_2O	10.0 %
CO_2	10.0 %
SO_2	0,10, 20, or 30 ppm
N_2	balance

1. The oxygen composition was switched between 0.2% O_2 and 1.0% O_2 every second.

Table 2. Isothermal Stoichiometry Scan Test

Gas Component	Concentration
O_2	0.20 % (net) to 1.0% (net)[1]
propylene (or propane)	300 ppm
CO	0.77 %
NO	500 ppm
H_2	0.2 % variable
H_2O	10.0 %
CO_2	10.0 %
SO_2	0,10, 20, or 30 ppm
N_2	balance

1. During this test, the oxygen composition was switched between a value lower than net and a value greater than net. During the scan, both values increase such that the net oxygen composition is increased from 0.2% to 1.0% in steps.

Additional tests were performed in which the net stoichiometry was scanned

from a net reducing feedstream (A/F = 14.1) through stoichiometry (A/F = 14.6) to a net oxidizing feedstream (A/F = 15.1) at a given catalyst temperature. This test, sometimes called an A/F ratio sweep test, closely models the exhaust of a late model 3.8 L V-6 engine operating under closed-loop control (the gas composition used for this test is listed in Table 2). During this test, a cycling amplitude of ± 0.5 A/F and a cycling frequency of 0.5 Hz was used. These tests were performed to determine the impact of sulfur on catalyst activity as a function of feedstream stoichiometry. The exhaust gas concentrations and conditions used for all three of these tests are discussed in more detail elsewhere [35-37].

3.RESULTS AND DISCUSSION

3.1 Effect of Sulfur on Lightoff

The effect of sulfur dioxide on lightoff at stoichiometry of the thermally aged 0.29 % Pd catalyst is shown in Figures 1 and 2 using propylene and propane, respectively, to represent the hydrocarbon in the simulated exhaust feedstream. For the purpose of this work, lightoff activity is defined as the temperature at which 50% conversion efficiency occurs for a particular reactant. The lightoff activity was first obtained using a feedstream with no sulfur dioxide added. This experiment was repeated several times, using a different concentration of sulfur dioxide in the feedstream with each experiment. Lightoff activities were thus obtained using 10 ppm, 20 ppm, and 30 ppm sulfur dioxide. These particular sulfur concentrations were chosen as they represent realistic sulfur levels in current available fuels, approximately 150 ppm, 300 ppm, and 450 ppm, respectively [35,36]. As will be discussed later, each experiment was followed by a high temperature treatment in which the SO_2 was removed from the feedstream, and the sample temperature was increased to 700°C where it remained for 30 min, followed by cooling to 500°C. This treatment was found to restore the catalytic activity to the level originally measured prior to exposure to any SO_2.

The results obtained using either propylene or propane consistently show an increase in lightoff temperatures of HC, CO and NOx as the sulfur content in the feedstream is increased. The magnitude of the increase in the propylene and CO lightoff temperatures was on the order of 40°C as the SO_2 content was increased from 0 ppm to 30 ppm, while the increase in the propane and CO lightoff temperatures was on the order of 60°C for the same increase in SO_2 concentration. Regardless of the type of hydrocarbon used, the increase in the lightoff temperature of HC and CO appeared to be non-linear with increasing sulfur concentration: most of the increase in the lightoff temperature occurred when the SO_2 concentration was increased from 0 ppm to 10 ppm, while a

smaller increase in the lightoff occurred with further increase in the SO_2 concentration from 10 ppm to 30 ppm. The NOx activity was markedly lower than HC or CO, and adding even small amounts of SO_2 resulted in the failure to reach the 50% conversion efficiency over the range tested (200 to 500°C). However, in comparing the activity profile over this temperature range, one can conclude that the NOx activity was also significantly affected by the presence of SO_2. We note that upon adding 10 ppm of SO_2 to the simulated exhaust, not only the beginning of the catalyst lightoff was increased (by roughly 40°C using propylene and 60°C using propane), but the warmed-up activity at 500°C was also decreased by roughly a factor of 2 using either hydrocarbon when the SO_2 concentration was increased from 0 ppm to 30 ppm. For NOx, most of the increase in the beginning of lightoff occurred upon increasing the SO_2 level from 0 ppm to 10 ppm, whereas further increases in SO_2 resulted in smaller increases in the temperature at which lightoff begins. Although not indicated in the figures, the magnitude of the effect of SO_2 on lightoff activity is **larger** than the effect of the thermal aging procedure on activity. The thermal aging procedure used in this study has been found to generally cause a 30-35°C increase in CO and HC lightoff temperature.

Similar lightoff tests were performed with the thermally aged 0.13% Pt, 0.0093% Rh production catalyst. In this case, the results obtained using either propylene (Figure 3) or propane (Figure 4) also consistently show an increase in lightoff temperatures of HC, CO and NOx as the sulfur content in the feedstream was increased. The magnitude of the increase in the propylene, CO, and NOx lightoff temperatures was on the order of 40°C as the SO_2 content was increased from 0 ppm to 30 ppm. When propane was used as the hydrocarbon, the increase in the propane lightoff temperature was on the order of 40°C while the increase in the CO and NO_x lightoff temperature was on the order of 60-70°C for the same increase in SO_2 concentration. Regardless of the type of hydrocarbon used, the increase in the lightoff temperature of HC and CO was also found to be non-linear with increasing sulfur concentration. For experiments conducted using propylene for the hydrocarbon, nearly all of the increase in the lightoff temperature occurred when the SO_2 concentration was increased from 0 ppm to 10 ppm: further increases in the SO_2 level up to 30 ppm resulted in very little additional increase in the lightoff temperature. For experiments in which propane was used, the increase in the lightoff temperature with but still very non-linear. Although not indicated on the figures, we note that the effect of sulfur on the lightoff performance was comparable to the effect due to the thermal aging treatment used in this work.
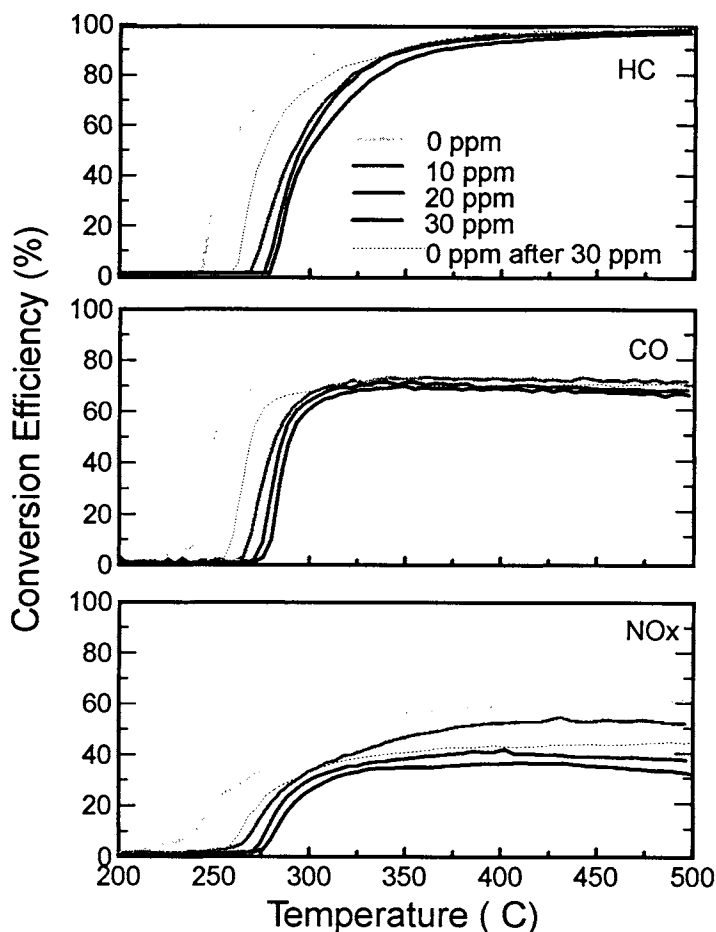
Figure 1. Lightoff curves for a thermally aged Pd catalyst sample using propylene as a hydrocarbon surrogate. Each curve was obtained using a different sulfur dioxide concentration in the synthetic exhaust feedstream. The dashed line was the result of a lightoff test using 30 ppm sulfur dioxide in the feedstream which was repeated using 0 ppm sulfur dioxide in the feedstream.
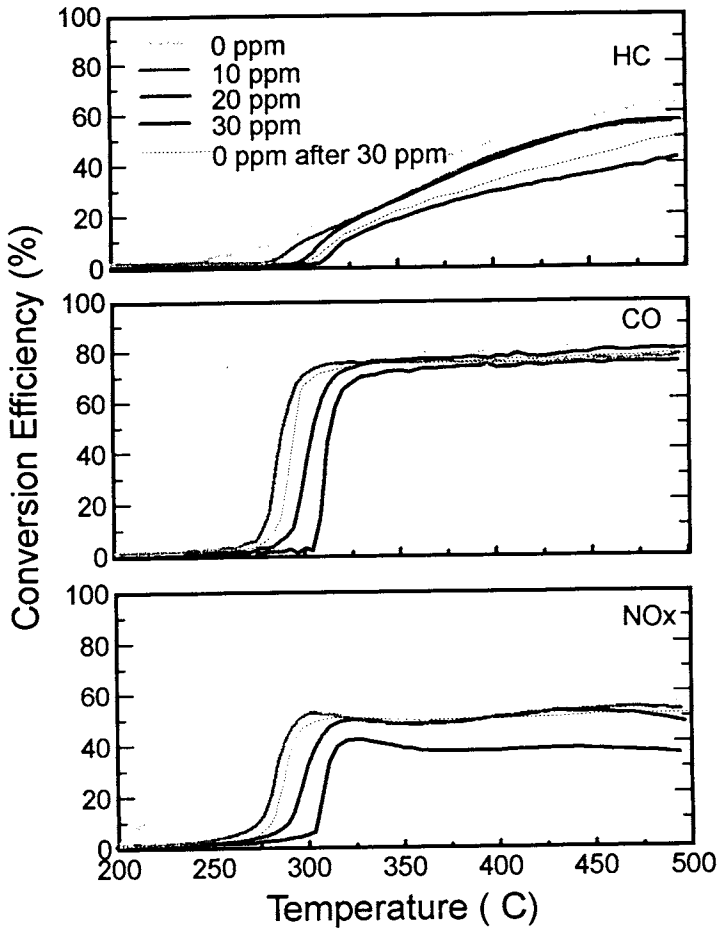
Figure 2. Lightoff curves for a thermally aged Pt-Rh catalyst sample using propylene as a hydrocarbon surrogate. Each curve was obtained using a different sulfur dioxide concentration in the synthetic exhaust feedstream. The dashed line was the result of a lightoff test using 30 ppm sulfur dioxide in the feedstream which was repeated using 0 ppm sulfur dioxide in the feedstream.

Because the Pt-Rh catalyst formulation was intended for positioning in an underfloor location in the vehicle, it is therefore not optimized for high temperature operation, and the high temperature aging treatment we used may have deteriorated the performance of the commercial Pt-Rh catalyst to a greater degree than the performance of the Pd catalyst, which has been formulated for operation at higher temperatures. Even considering this potential difference in the

aged catalysts, a comparison of the lightoff performance of the thermally Pd catalysts vs. the Pt-Rh catalyst with no sulfur in the feedstream does point out a clear advantage of the Pd catalyst for reducing cold-start alkene hydrocarbon and CO emissions. Although the Pt-Rh catalyst shows better lightoff performance for alkane hydrocarbons in this comparison, the alkenes figure more prominently in the contribution to overall NMOG since they are more abundant and have higher reactivity factors; this is one of several reasons why Pd-based catalyst technology holds promise for use in close-coupled converter applications.

We note with interest that the non-linear relationship between the SO_2 concentration and the magnitude of the impact on lightoff performance for both Pd and Pt-Rh based catalysts is characteristic of the effect of sulfur on monolithic three-way catalysts observed in previously reported laboratory [26] and vehicle studies [24]. Both studies showed that as the sulfur content was increased, the degradation in the lightoff or warmed-up emissions increased at a high rate initially, but became more gradual at higher sulfur levels, suggesting that very small amounts of sulfur in the exhaust can have a significant effect on emissions. In a more recent laboratory study, the relationship between the concentration of SO_2 and the magnitude of the effect on the activity of model Pd catalysts (Pd supported on alumina alone or in the presence of one promoter such as ceria or lanthana) was found to be linear for CO and HC activity, although we note that the model catalysts used in that study were pelleted, not monolithic. Differences in mass transfer effects and the distribution of noble metals in pelleted vs. monolith catalysts may account for the linear effect of sulfur on pelleted catalysts vs. the non-linear effect of sulfur in monoliths. We note that the vehicle studies, in which the non-linear effect was also observed, were also conducted primarily with monolith catalysts.

For all of the aged catalysts, an additional lightoff experiment was performed with no SO_2 in the feedstream following the lightoff experiment using 30 ppm SO_2. The results, shown in dashed lines in Figures 1-4, shows a decrease in the lightoff temperatures from the 30 ppm SO_2 experiment for both Pd and Pt-Rh type catalysts, but only partial recovery of activity (relative to the catalyst prior to exposure to SO_2) has taken place with the Pd catalyst, whereas nearly complete recovery of the original activity has taken place with the Pt-Rh catalyst. This result, which was also observed in a prior study of the effect of SO_2 on model Pd catalysts [36], further emphasizes the non-reversibility of sulfur poisoning in Pd catalysts, even for a state-of-the-art formulation, compared to the complete reversibility of the effect of sulfur in Pt-Rh three-way catalysts. We have speculated that the non-reversible sulfur poisoning of Pd is related to a

direct reaction between adsorbed S and the supported Pd metal, perhaps leading to the formation of a surface PdS compound [36], or possibly migration of S into the bulk of Pd. We have obtained evidence for the latter in studies of SO_2 adsorption on Pd foils [39], but further study is needed to better understand this phenomenon.
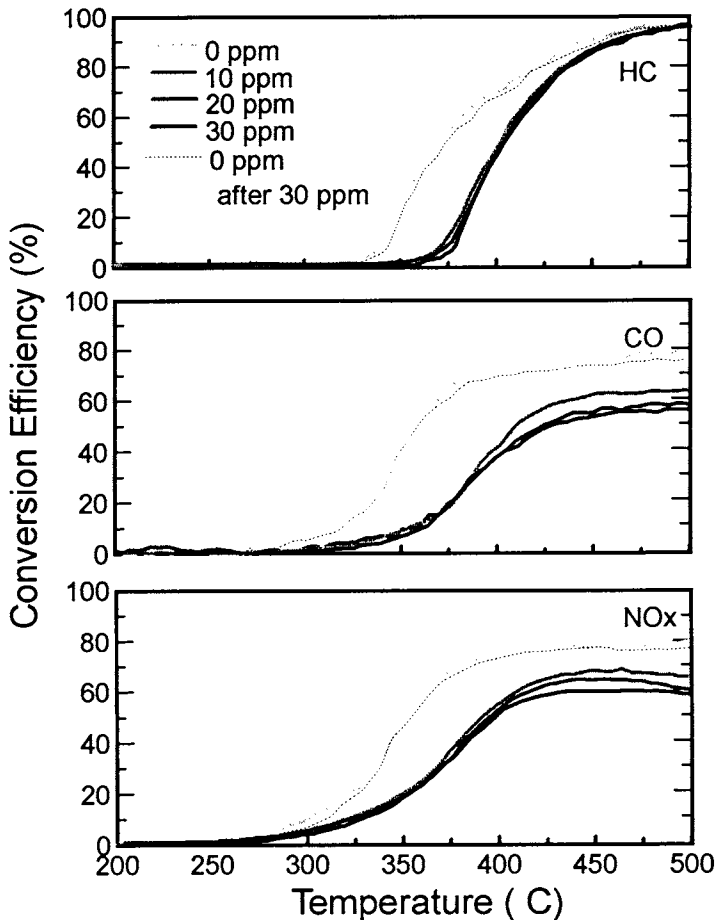

Figure 3. Lightoff curves for a thermally aged Pd catalyst sample using propane as a hydrocarbon surrogate. Each curve was obtained using a different sulfur dioxide concentration in the synthetic exhaust feedstream. The dashed line was the result of a lightoff test using 30 ppm sulfur dioxide in the feedstream which was repeated using 0 ppm sulfur dioxide in the feedstream.
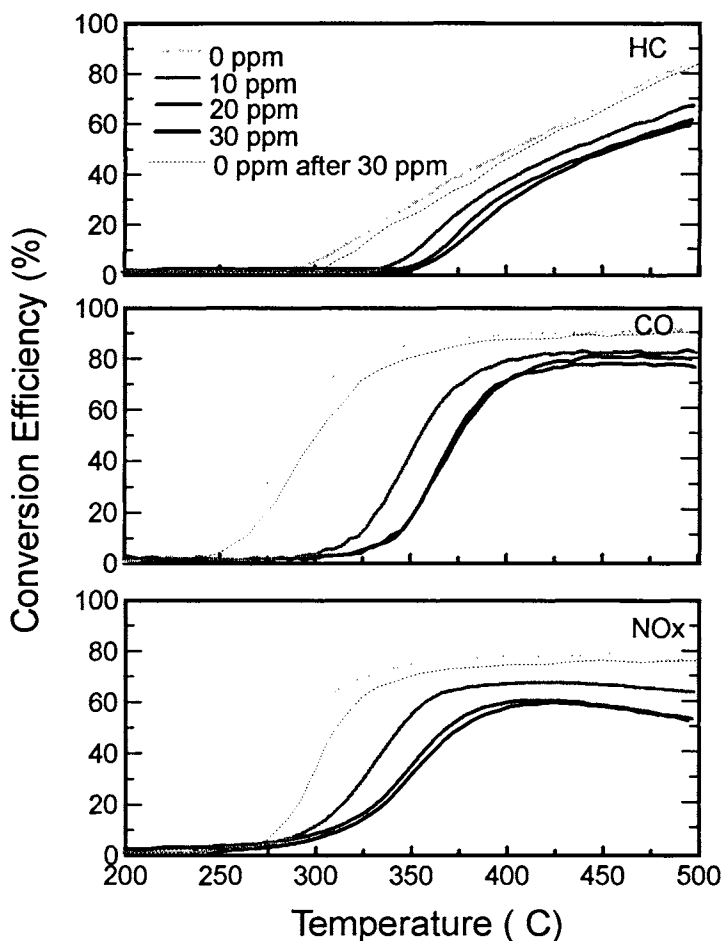
Figure 4. Lightoff curves for a thermally aged Pt-Rh catalyst sample using propane as a hydrocarbon surrogate. Each curve was obtained using a different sulfur dioxide concentration in the synthetic exhaust feedstream. The dashed line was the result of a lightoff test using 30 ppm sulfur dioxide in the feedstream which was repeated using 0 ppm sulfur dioxide in the feedstream.

3.2. Effect of Sulfur on Warmed-up Performance

The effect of sulfur dioxide on the isothermal (500°C), or "warmed-up" activity in which the exhaust was cycled about stoichiometry is shown in Figures

5 and 6 for thermally aged 0.29% Pd catalyst, first using propylene and then propane, respectively, to represent the HC in the exhaust. For this experiment, no SO_2 was present for approximately 5 min, then the SO_2 concentration was increased in a step-change to a desired level (10, 20 or 30 ppm) where it remained for 15 min. Following this, the SO_2 was removed from the feedstream and the activity measurement continued for an additional 25-35 min. This experiment was repeated several times, using a different concentration of sulfur dioxide in the feedstream with each experiment. Warmed-up activities were thus obtained using 10 ppm, 20 ppm, and 30 ppm sulfur dioxide. After each test, the SO_2 was removed from the feedstream, and the sample temperature was increased to 700°C where it remained for 30 min, followed by cooling to 500°C. This treatment was found to restore the catalytic activity to the level originally measured prior to exposure to any SO_2.

When propylene was used to represent the HC in this test (Figure 5) the results obtained for the 0.29% Pd catalyst indicate that when the sulfur level in the feed was increased, a gradual decrease in the activity was observed for HC, CO, and NOx. The absolute magnitude of the decrease was large for CO and NOx: an increase in the SO_2 concentration from 0 ppm to 30 ppm resulted in a decrease in CO conversion from 70% to 55% and in the NOx conversion from 65% to 30% after 15 min exposure to sulfur. Increasing the SO_2 concentration from 0 ppm to 30 ppm resulted in a decrease in the HC conversion from 98% to 95%, which in absolute magnitude does not appear to be as large an effect as with CO or NO_x, but we note that the 3% decrease in HC conversion translates into an increase in HC breakthrough of 150%. The rate of the decrease in conversion efficiency for HC, CO and NO_x slowed considerably after 15 min of exposure, but had not yet reached a stable level at this point.

When SO_2 was removed from the feedstream, the HC activity appeared to return to near its original level, but the recovery of CO and NO_x activity was incomplete, even following an exposure of 30 min in a "clean" feedstream. Although not shown, when the experiment was allowed to run for 3 h, very little additional recovery took place.

Similar experiments with the 0.29% Pd catalyst were performed using propane to represent the hydrocarbon (Figure 6). Again, a gradual decrease in the HC, CO, and NO_x activity was observed, although the rate of poisoning did not change during the 15 min exposure to sulfur in the feedstream, and therefore equilibrium was not achieved. Note also that the magnitude of the decrease in activity was significantly larger for propane than for propylene: for instance, exposure to 30 ppm SO_2 resulted in an 18% decrease in HC conversion, translating into a ~200% increase in HC breakthrough. Decreases in the CO (by 45%) and NOx (by 50%) were also more significant than that observed when
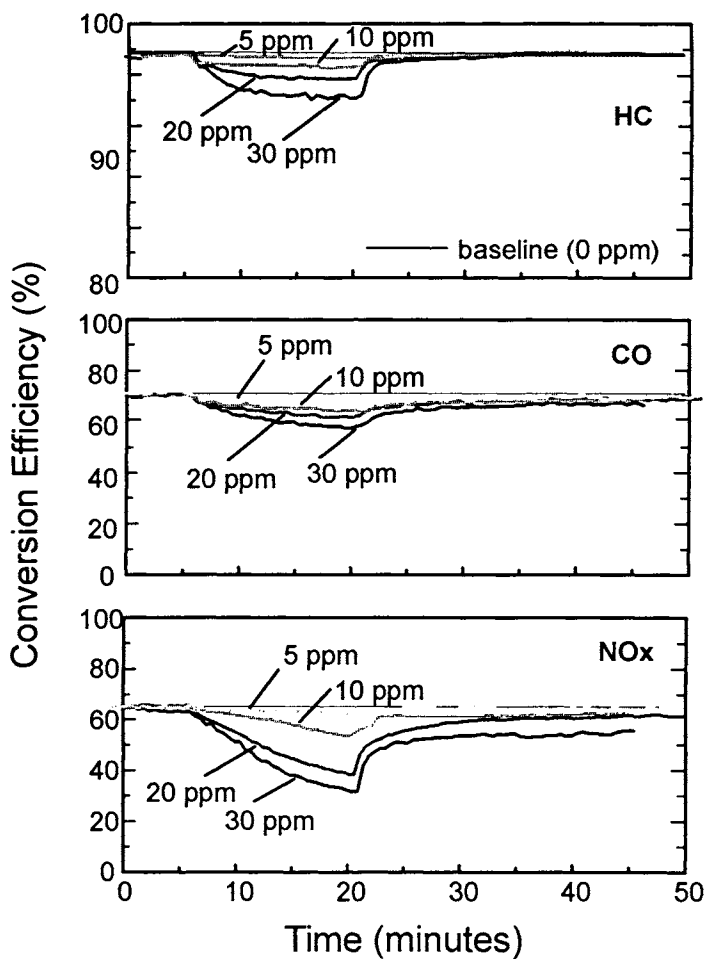
Figure 5. Isothermal (500°C) activity of the thermally aged Pd catalyst using propylene as a hydrocarbon surrogate. In these experiments, the sulfur dioxide concentration is maintained at 0 ppm for 5 min, then increased to either 5, 10, 20 or 30 ppm for 15 min, then decreased to 0 ppm for an additional 45 min.
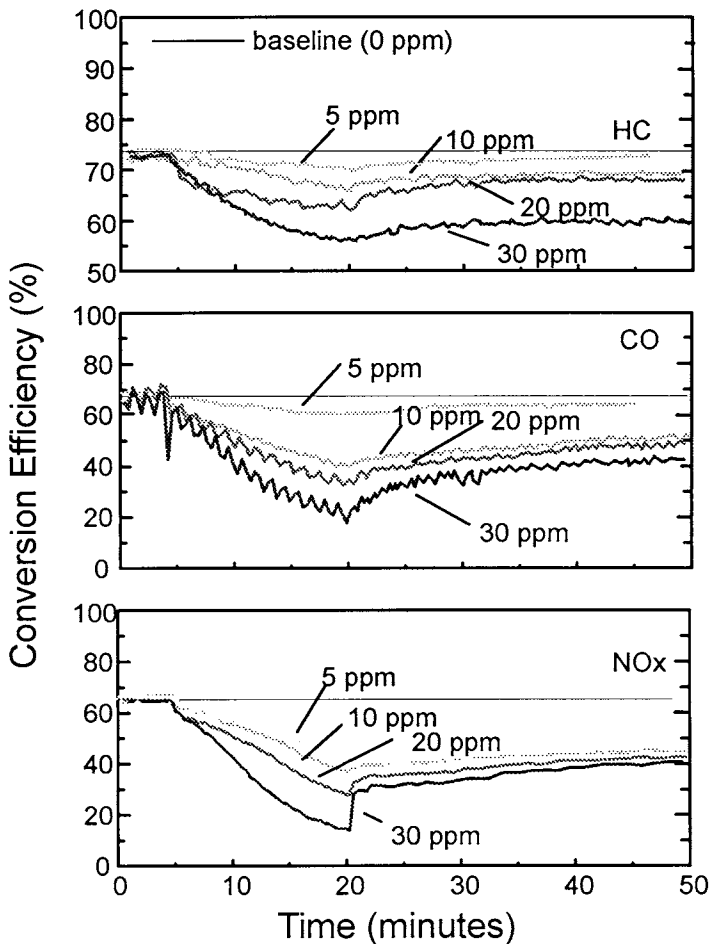
Figure 6. Isothermal (500°C) activity of the thermally aged Pd catalyst using propane as a hydrocarbon surrogate. In these experiments, the sulfur dioxide concentration is maintained at 0 ppm for 5 min, then increased to either 5, 10, 20 or 30 ppm for 15 min, then decreased to 0 ppm for an additional 45 min.

propylene was used to represent the hydrocarbon (15% and 40%, respectively). It is also important to point out that when sulfur was removed from the feedstream, very little recovery of activity took place, indicating that most of the poisoning is irreversible at this temperature. The reason for the absence of a change in the

poisoning rate over the 15 min exposure period together with the dominance of the irreversible poisoning has yet to be identified, but at present we attribute part of this effect to hydrocarbon coking of the catalyst which is promoted by the presence of SO_2 in the feedstream.

In Figure 7, we show the effect of SO_2 on the warmed-up activity of the thermally aged 0.13% Pt, 0.0093% Rh production catalyst using propylene to represent the hydrocarbon. For this catalyst, the presence of SO_2 in the feedstream resulted in a more instantaneous decrease in the HC, CO, and NO_x conversion efficiencies, but the magnitude of the decrease was dramatically lower than observed with the 0.29% Pd catalyst exposed to the same level of sulfur. For example, exposure to 30 ppm SO_2 resulted in a decrease of roughly 1% in the HC conversion, translating to an increase of 30% in HC breakthrough. Decreases of 20% in the CO, and 30% in the NO_x conversions were also observed. Moreover, when SO_2 was removed from the feedstream, near complete recovery of the activity occurred within 15-30 min. The relative instantaneous behavior of poisoning as well as the complete reversibility were found to be consistent with those of a similar laboratory study in which the effect of SO_2 on a three-way Pt-Rh commercial monolith catalyst was compared with the effect on a commercial Pt-Pd-Rh pelleted catalyst [26].

Finally, in Figure 8 we show the effect of SO_2 on the warmed-up activity of the thermally aged 0.13% Pt, 0.0093% Rh production catalyst using propane to represent the hydrocarbon. For this case, the presence of sulfur at 30 ppm resulted in a larger decrease in the HC conversion efficiency, from 86% to 68%, translating into an increase in HC breakthrough of ~200%, while the impact on the conversion efficiencies of CO (97% to 80%) and NOx (92% to 75%) was smaller than when propylene was used as the hydrocarbon. Removal of sulfur from the feedstream did lead to recovery of most (~60%-70%) but not all of the original activity after exposure to a sulfur-free feedstream for 30 min. The incomplete recovery of activity observed with both the Pd and Pt-Rh commercial samples when propane was used as the hydrocarbon suggests coking of the catalyst is important. Further evidence for this rationalization was obtained by observing that treatment of the Pt-Rh catalyst in a net lean (1% O_2) feedstream at 700°C resulted in near complete recovery of activity. Similar treatment of the propane-exposed Pd catalyst resulted in partial recovery of activity, whereas subsequent treatment in a net rich feedstream at 700°C resulted in complete recovery of the original activity. Our findings that SO_2 enhances hydrocarbon coking (when propane is present in the feedstream) is consistent with earlier reports that SO_2 can increase the acidity of supports such as alumina, and thus enhance the role of this support as an acid catalyst in hydride abstraction from alkanes such as propane, which then leads to a number of different reactions

including polymerization and further dehydrogenation. The resulting carbonaceous material is partially hydrogenated (so called "reversible" coking [40]) since it can be removed by oxidation. This coking phenomenon has been commonly observed on acid catalysts used for steam reforming [41,42].

3.3 Effect of Sulfur on Performance as a Function of Stoichiometry

Both thermally aged catalysts were evaluated using tests in which the net stoichiometry was scanned from a net reducing feedstream through stoichiometry to a net oxidizing feedstream at a catalyst temperature of 500°C. These tests were first performed without sulfur in the feedstream and then repeated with 30 ppm SO_2 in the feedstream to determine the impact of sulfur on catalyst activity as a function of stoichiometry.

Figure 9 shows the HC, CO and NO_x conversion efficiencies for the aged 0.29% Pd catalyst as a function of mean air/fuel ratio at 500°C using a test in which the net stoichiometry was scanned from a net reducing feedstream through stoichiometry to a net oxidizing feedstream. For this case, propylene was used to represent the hydrocarbon. These tests were performed first with no SO_2 and repeated with 30 ppm SO_2 in the feedstream. In the oxidative, or 'lean" exhaust environment between mean A/F ratios of 15.1 to 14.7, the presence of SO_2 results in a slight decrease in the conversion efficiency for HC, CO and NO_x. Below a value of 14.7, the presence of sulfur results in a slight decrease in the CO activity which continues until a rich extreme of 14.1 in A/F ratio. The effect of SO_2 on the conversion efficiencies of HC and NO_x, however, was significant below an A/F ratio of 14.7 and increases with decreasing mean A/F until the "rich" extreme of 14.1 was reached. Thus, the degree of the impact of sulfur on HC and NO_x conversion efficiency is greatest under stoichiometric and "rich" operating conditions. The maximum impact of 30 ppm SO_2 in terms of breakthrough in HC and NO_x occurred at a mean A/F ratio of 14.3 to 14.2. At this point, the HC breakthrough increased by 600-700% while the NO_x breakthrough increased by 400-500%. This behavior was also observed in a similar study of the effect of SO_2 on model Pd three-way catalysts [36] and is consistent with suggestions that SO_2 directly poisons the noble metal surface in rich conditions [13].

Figure 10 shows the HC, CO and NO_x conversion efficiencies for the thermally aged 0.29% Pd catalyst as a function of mean air/fuel ratio at 500°C using propane to represent the hydrocarbon. For reasons stated earlier, the extent of the effect of sulfur on catalyst activity was difficult to determine due to the inability to reach equilibrium when sulfur was added to the feedstream.
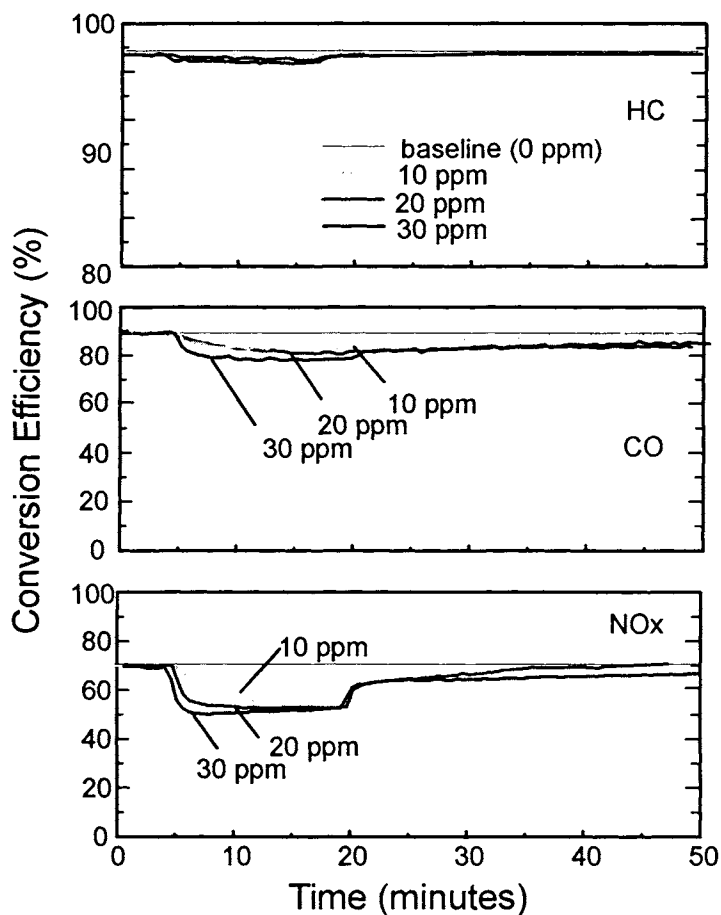
Figure 7. Isothermal (500 °C) activity of the thermally aged Pt-Rh catalyst using propylene as a hydrocarbon surrogate. In these experiments, the sulfur dioxide concentration is maintained at 0 ppm for 5 min, then increased to either 5, 10, 20 or 30 ppm for 15 min, then decreased to 0 ppm for an additional 45 min.
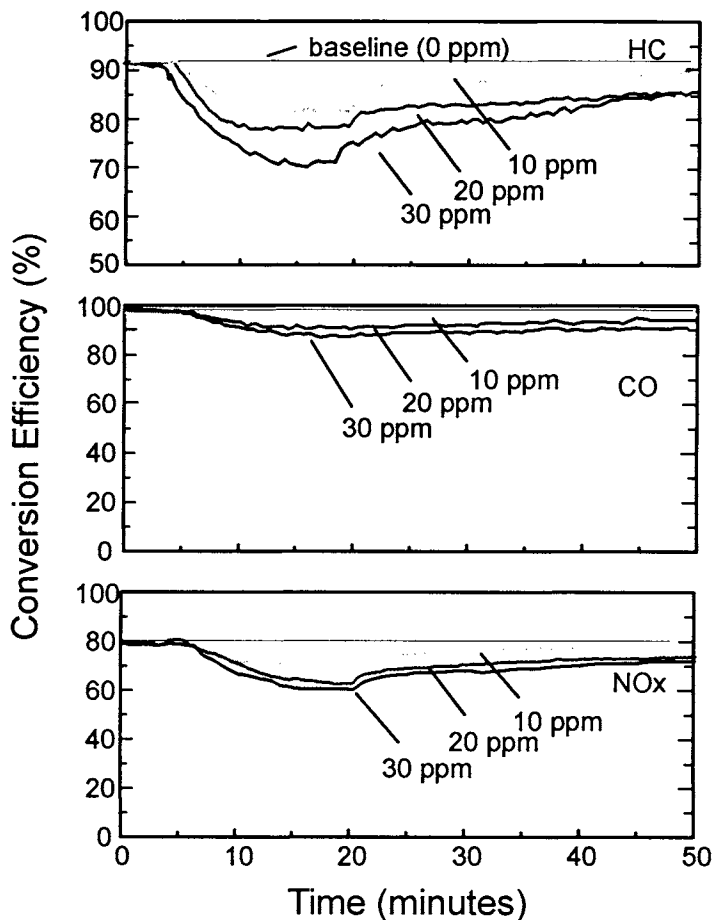
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Figure 8.   Isothermal (500°C) activity of the thermally aged Pt-Rh catalyst using propane as a hydrocarbon surrogate. In these experiments, the sulfur dioxide concentration is maintained at 0 ppm for 5 min, then increased to either 5, 10, 20 or 30 ppm for 15 min, then decreased to 0 ppm for an additional 45 min.

Consequently, when 30 ppm SO_2 was added to the feedstream, the A/F ratio scan experiment was repeated several times until the result was found to reproducible within 5%, but we note that the full impact of sulfur on activity is probably larger. As indicated in the figure, we also found that the first scan from a lean to rich A/F

ratio produced a different result in the propane conversion than a first scan from a rich to lean A/F ratio when SO_2 was present. Repeated A/F ratio scans resulted in the lower curve showing relatively constant propane conversion of 40-50% over the entire A/F ratio range tested. Thus, operation in a rich exhaust containing propane and SO_2 results in an additional poisoning effect which is only evident during operation in a stoichiometric to lean environment, and which cannot be reversed at 500°C. We attribute this particular effect to SO_2-induced coking of the Pd catalyst in rich conditions: treatment in lean conditions with no sulfur in the feedstream results in significant recovery of activity in the lean A/F ratio region, but not in the rich A/F ratio region. We also found that the presence of SO_2 resulted in a slight decrease in the CO conversion and a significant decrease in the NO_x conversion in rich conditions, but the coking effect noticed in the HC activity did not significantly affect CO and NO_x activity. This observation suggests that the active site participating in the oxidation of propane differs from those sites catalyzing the oxidation of CO and reduction of NO

Turning now to the thermally aged 0.13% Pt, 0.0093% Rh production catalyst, we show the HC, CO and NO_x conversion efficiencies as a function of mean A/F ratio at 500°C using propylene to represent the hydrocarbon in Figure 11. It is interesting to note that for this catalyst, the effect of adding 30 ppm SO_2 is generally similar to the Pd catalyst: the HC and NO_x conversion efficiencies were significantly decreased in rich conditions, while the CO conversion efficiency was only moderately decreased, but again in rich conditions. With no sulfur present, it is interesting to note that in lean and stoichiometric conditions, the propylene conversion efficiency was slightly lower for the Pd catalyst in comparison to the Pt-Rh catalyst, while the Pd catalyst was significantly more active than the Pt-Rh catalyst for propylene oxidation in rich conditions, between 14.6 and 14.1 in mean A/F ratio units. This hydrocarbon activity advantage of the Pd over Pt-Rh was completely canceled when 30 ppm SO_2 is present in the feedstream, and became a disadvantage when sulfur was removed from the feedstream, as the Pt-Rh catalyst recovered all of its original activity (not shown in the figure), but the Pd catalyst did not. The rapid decrease in HC activity in extreme A/F ratio conditions (between 14.2 and 14.1) and that the presence of sulfur does not significantly affect the activity in this region. We also note that with 30 ppm SO_2 present, the decrease in the NO_x activity of the Pt-Rh catalyst was not as large as the decrease in the NO_x activity observed with the Pd catalyst. This result is consistent with the reported relative resistance of Rh to direct sulfur poisoning [13].
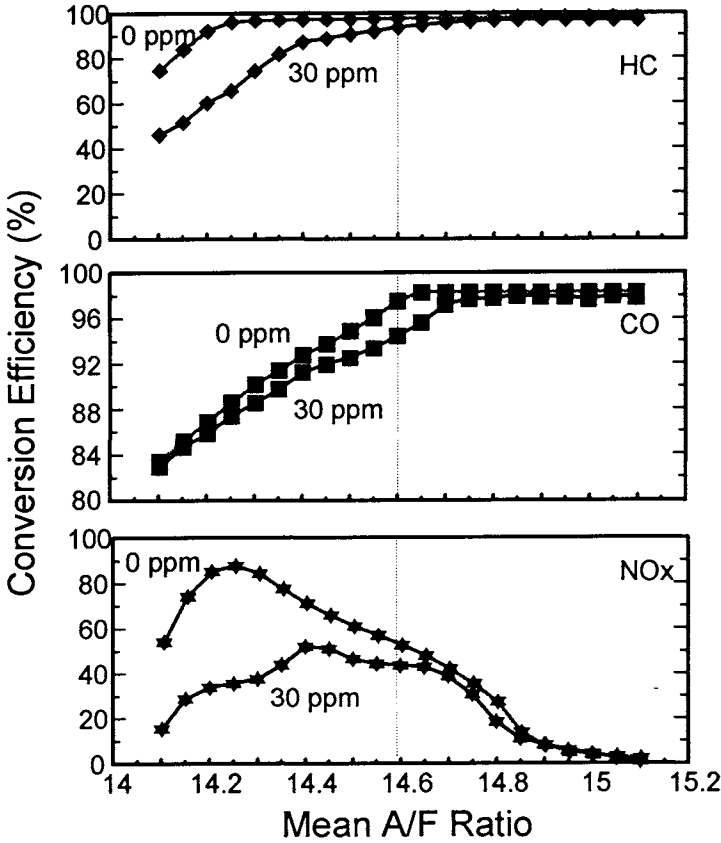
Figure 9. Effect of sulfur dioxide on the activity of thermally aged Pd in a cycled stoichiometric exhaust as a function of mean air/fuel ratio using propylene as a surrogate hydrocarbon.

The HC, CO and NO_x conversion efficiencies for the thermally aged 0.13% Pt, 0.0093% Rh catalyst as a function of mean air/fuel ratio at 500°C were again determined except that propane was used to represent the hydrocarbon. The result is shown in Figure 12 first with no SO_2, then with 30 ppm SO_2 in the feedstream. The effect of sulfur on catalyst activity followed a similar trend as with the previous case: the HC and NO_x activity was reduced in stoichiometric and rich conditions, although the HC activity was not significantly affected at extreme rich conditions of 14.2 to 14.1 in A/F ratio. The CO conversion

efficiency was also similarly affected, being moderately reduced in rich conditions
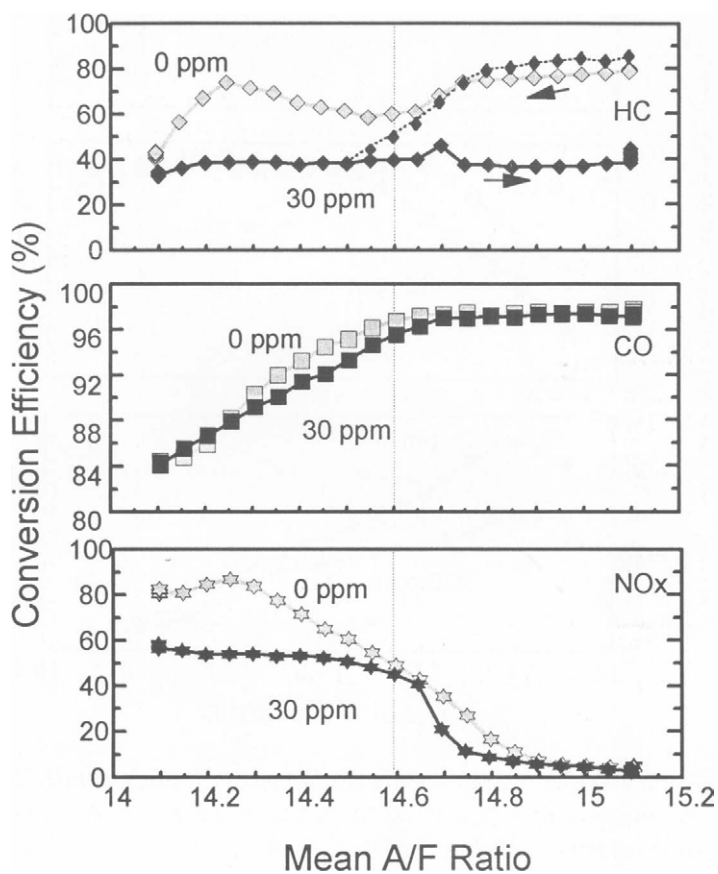

Figure 10. *Effect of sulfur dioxide on the activity of thermally aged Pd in a cycled stoichiometric exhaust as a function of mean air/fuel ratio using propane as a surrogate hydrocarbon.*

. Note that the magnitude of the effect of sulfur on the overall activity of the Pt-Rh catalyst was not as large as the effect on the Pd catalyst, particularly with regard to the HC conversion.
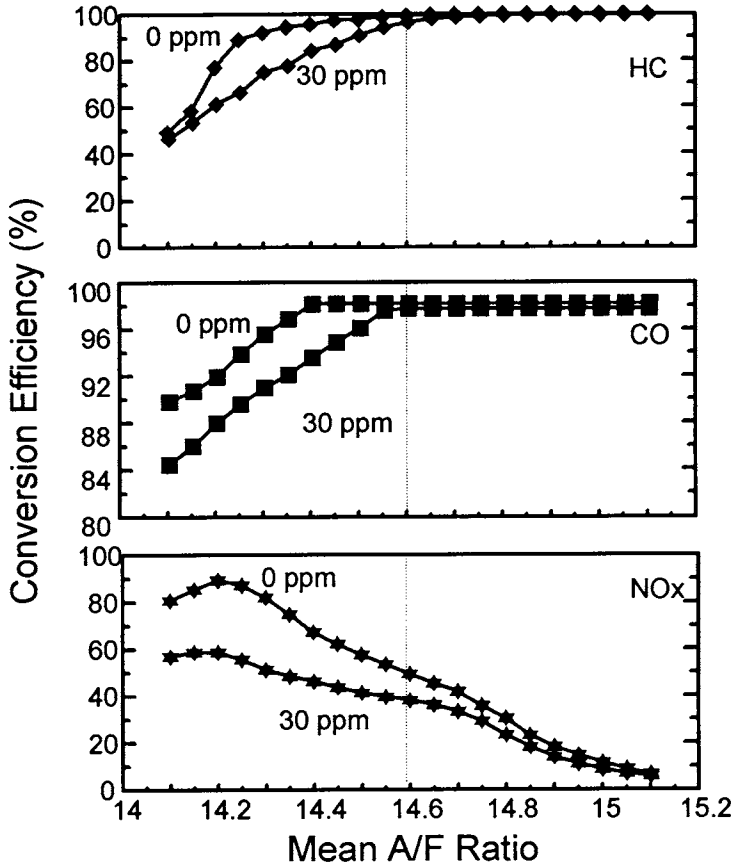
Figure 11. Effect of sulfur dioxide on the activity of thermally aged Pt-Rh in a cycled stoichiometric exhaust as a function of mean air/fuel ratio using propylene as a surrogate hydrocarbon.

There is one exception in these results using propane relative to those obtained when propylene was used to represent the hydrocarbon: in extremely lean conditions, the HC activity was enhanced by the presence of SO_2: this effect has been reported in previous laboratory studies of propane oxidation [26]. We suggested previously that SO_2 promotes acid catalysis of propane dehydrogenation, only in this case, the carbonaceous material may be more easily removed from Pt-Rh than from Pd under oxidizing conditions, thus complete oxidation of propane dominates over coking. Other factors, however, may also be

responsible for these observations due to a number of differences in the properties of the two catalysts. For example, the dispersion of the Pt-Rh catalyst is generally significantly greater than the Pd catalyst, and it has been shown that highly dispersed noble metals are less likely to be poisoned by coke formation than similar catalysts with lower noble metal dispersion [43]. Certainly, further study is needed to gain a better understanding of this phenomenon.
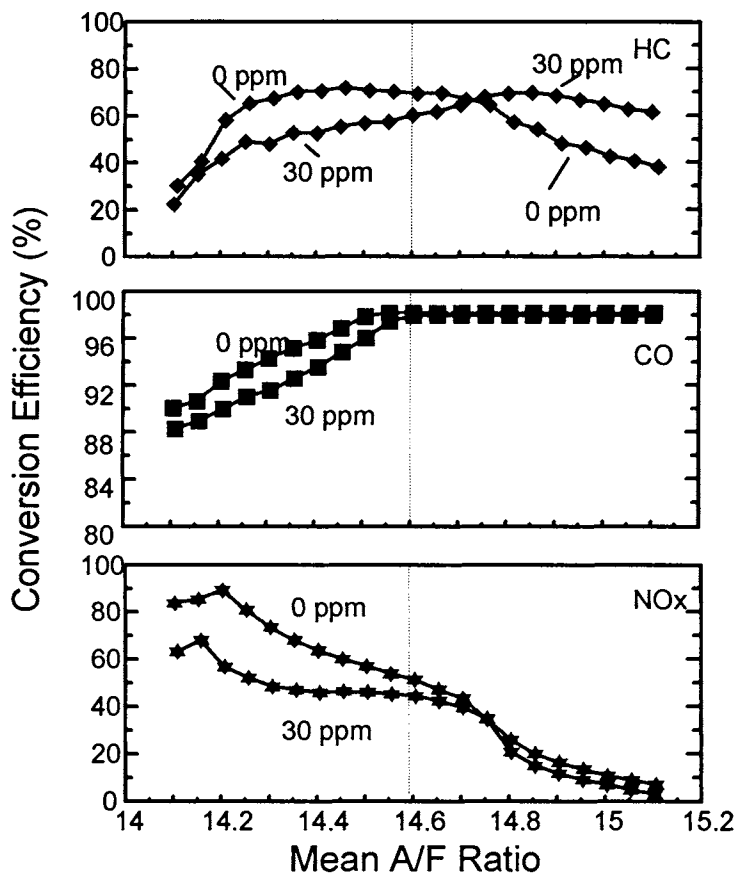

Figure 12.   Effect of sulfur dioxide on the activity of thermaly aged Pt-Rh in a cycled stoichiometric exhaust as a function of mean air/fuel ratio using propane as a surrogate hydrocarbon.

4. SUMMARY

In this work, we have compared the effect of SO_2 on the three-way performance of a commercially prepared, thermally aged Pd three-way catalyst with that of a commercially prepared, thermally aged Pt-Rh three-way catalyst. The results obtained in the present study were generally consistent with previous laboratory studies of commercially prepared Pt-Rh catalysts [26] and model Pd three-way catalysts [36]. We found that an increase in the sulfur content in simulated cycled stoichiometric exhaust resulted in a loss of both lightoff and warmed-up activity. The magnitude of the impact of sulfur on lightoff activity of both Pd and Pt-Rh catalysts was comparable when propylene was used for the hydrocarbon contribution to the exhaust, and larger but still comparable when propane was used to represent the hydrocarbon in exhaust. The Pd catalyst showed generally better lightoff activity than the Pt-Rh catalyst regardless of the sulfur content in the feedstream, but the opposite was valid when propane was used to represent the hydrocarbon. Under warmed-up conditions, the loss of activity for HC, CO and NO_x due to the presence of sulfur was greater under slightly rich conditions than under lean conditions for both Pd and Pt-Rh catalysts, while the magnitude of the impact on propylene and NO_x activity under warmed-up stoichiometric conditions was significant greater for the Pd catalyst than for the Pt-Rh catalyst. When propane was used to represent the hydrocarbons in exhaust, the impact of sulfur on the HC conversion was comparable for both catalysts, although the impact on CO and NO_x was greater for Pd than for Pt-Rh. Finally, we found that when propylene was used for the hydrocarbon, the effect of SO_2 on the activity of the Pd catalyst was partly irreversible under the conditions used in this study, while the effect on Pt-Rh was completely reversible. When propane was used to represent the hydrocarbon, the effect on the activity of both catalysts was partly irreversible, but the magnitude of the irreversible poisoning was larger on Pd. Part of the irreversible poisoning effect is attributed to a direct interaction or reaction between SO_2 and Pd, while the other part is attributed to the promotional effect of SO_2 in hydrocarbon coking of the catalyst when alkane hydrocarbons are present.

5. ACKNOWLEDGMENT

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