

SUPPORT EFFECTS ON PALLADIUM CATALYSTS FOR METHANOL FUEL APPLICATIONS

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ABSTRACT

Methanol, formaldehyde, carbon monoxide, and propylene conversion were examined in a laboratory flow reactor over three base-metal containing alumina-supported palladium (Pd) catalysts in addition to Pd on γ -alumina catalyst. The base metals were cerium, barium, and a combination of the two. Experiments were performed to determine the effect of air to fuel ratio on lightoff temperatures of various feed components for the base-metal catalysts as compared to Pd on γ -alumina. For a vehicle operating at fuel-rich or stoichiometric conditions, the cerium containing catalyst gave the best overall performance among those tested. However, at lean conditions, all the catalysts had similar performance.

Keywords: Methanol Oxidation, Palladium Catalyst, Base Metals

INTRODUCTION

Methanol is a strong candidate as an alternative fuel to gasoline. Since methanol is essentially free of contaminants such as lead and sulfur, it has an advantage over gasoline in minimizing the poisoning of catalysts used for emissions control. In addition, methanol exhaust does not contain many of the hydrocarbon species present in gasoline exhaust. Methanol exhaust is composed primarily of unburned methanol, formaldehyde, carbon dioxide, and small amounts of hydrocarbons generated when methanol is used as a mixture with gasoline. The major components that are cause for concern are the photochemically active formaldehyde and the unburned methanol.

Unburned methanol is of particular importance during cold-start conditions where a vehicle

usually operates under fuel-rich conditions to improve driveability. Methanol levels in the exhaust during cold-start conditions can be as high as 0.9 volume percent as compared to 0.04 volume percent during normal operation (McCabe, et al., 1990). With the passage of the Clean Air Act, further tightened restrictions on exhaust emissions have resulted in extensive research on the design of catalysts that will reduce emissions from a methanol-fueled vehicle.

McCabe and coworkers (McCabe, et al., 1986) investigated the effect of feed stream composition and reactor temperature on methanol oxidation. Among the catalysts tested, rhodium (Rh), silver (Ag), and copper (Cu) were found to be much less active than either platinum (Pt) or palladium (Pd) (McCabe, et al., 1986). However, the presence of carbon monoxide had

little effect on the oxidation of methanol over these catalysts, while significantly affecting the Pt and Pd catalysts and raising the lightoff temperature for methanol over both catalysts. As a consequence, low temperature methanol oxidation activities of the Ag and Cu catalysts were as good or better than those of Pt or Pd in the presence of carbon monoxide (CO). This is consistent with weak chemisorption of CO compared to methanol on Ag and Cu surfaces, as observed in previous work (Ryberg, 1982; Madix, 1980). Also, the Ag displayed a high selectivity to complete oxidation; in particular, the Ag catalyst provided the lowest formaldehyde yield of all catalysts (McCabe, et al., 1986).

Additional studies by McCabe, et al., (1986) have investigated the kinetics of methanol oxidation on a Pt wire in a flow reactor at low ($3e-4$ atm) pressure. The proposed mechanism involves a major pathway responsible for approximately 99 percent of methanol oxidation and a minor pathway that accounts for the remaining 1 percent. The proposed mechanism is illustrated in Figure 1.

Automotive catalysts for gasoline powered vehicles generally include palladium or platinum. Palladium, which is less expensive than platinum, is subject to poisoning by the sulfur present in gasoline (Kummer, 1986). Methanol fuels generally have very little sulfur, thus Pd only catalysts may be a viable option for alternative-fuel vehicles. In addition, recent experiments have shown extended durability for Pd-only catalysts in engine-aging studies (Summers, et al., 1989). Pd, which is the least expensive noble metal, is also the preferred noble metal for C_1 and C_2 hydrocarbon conversions. Palladium's viability as an option for a methanol-fuel vehicle exhaust catalyst provides the impetus to investigate methanol oxidation over palladium-only catalyst formulations.

This paper presents the results of our experimental evaluation of the performance of two base-metals when incorporated into the washcoat of a palladium monolith catalyst. All results are compared to a palladium-only (Pd) catalyst with an alumina washcoat and no base-metal present. Experiments were conducted in a laboratory flow reactor with a feed gas chosen to simulate exhaust from a

methanol-fuel vehicle. All catalysts were tested fresh as supplied by the manufacturer. The effect of oxygen to fuel ratio on the lightoff temperatures of methanol, formaldehyde, carbon monoxide, and propylene was examined. Within this paper, we report on the performance of each catalyst at varying oxygen and methanol concentration. The effects of variation in the washcoat formulation were determined and analyzed in terms of an appropriate reaction description.

EXPERIMENTAL

Laboratory catalyst evaluations were carried out in a stainless steel flow reactor system shown in Figure 2. Catalyst samples were 1 inch in diameter by 0.5 inch long cylindrical sections of ceramic monolith wrapped with an inert fiberglass paper to eliminate void space between the catalyst and reactor wall. The reactor and process lines were heated with Thermolyne heating tapes, and the reactor temperature was monitored with a type J thermocouple placed against the center of the effluent side of the catalyst. Control of the reactor temperature was achieved with a solid state power controller.

Feed gases were supplied via gas cylinders fitted with pressure regulators and individual gas flow rates were controlled with rotameters. Methanol, formaldehyde, and water were introduced into the feed as liquid and vaporized upon mixing with the heated gas feed. Liquid flow rates were controlled with the combination of a metering valve and a rotameter. The liquid feed was injected into the process stream through a septum port just after the pre-heater of the process gases (Figure 2) and the feed stream passed upward through the catalyst. The pre-heater served to increase the temperature of the feed stream gases sufficiently to insure vaporization of the liquid feed. Temperature at the point of injection of the liquid was measured with a type J thermocouple.

Feed samples were taken at the reactor effluent at low temperature with very little or no conversion (as determined by the partial pressure of CO_2). Conversion of the feed components was measured via off-gas analysis of the effluent stream with a Dycor M200 Series Quadrupole

Gas Analyzer. Data was first taken in analog mode which allowed scanning of a wide (0-100 AMU) mass range to insure there were no unforeseen products, and then in tabular mode, which scans a maximum of twelve pre-selected AMU. Data was recorded in the form of partial pressures and conversion to molar flow rates was accomplished by calibration of each component's response factor with standard gas mixtures. Response factors of the individual gases were measured relative to a standard gas. Deconvolution of the mass spectral data was accomplished using the spectral library supplied by the manufacturer.

Experiments were performed over the range 100-400 °C at varying oxygen and methanol concentration. Data points were taken every 6-7 °C to insure identification of the lightoff temperature within a narrow range. Space velocities in all cases were approximately 13,000 h⁻¹ (volume basis; standard conditions). The Oxygen:Fuel ratio was calculated as :

$$\lambda = \frac{F_{O_2}}{\left(\frac{1}{2}F_{MeOH} + \frac{1}{2}F_{CO} + \frac{1}{2}F_{(C_2H_6)}\right)}$$

where F_i is the molar flow rate of component (i). The oxygen to fuel ratio was manipulated by altering the oxygen content in the feed.

Four different Pd-only catalysts supported on a γ -alumina washcoat on a ceramic monolith were evaluated fresh: 1) Pd-alumina with no base-metal, 2) Pd-alumina with barium, 3) Pd-alumina with cerium, and 4) Pd-alumina with both barium and cerium. All catalysts were supplied by Allied Signal, Inc. Each catalyst sample was preconditioned in a rich ($\lambda < 1$) feed at 350°C for one hour to eliminate any oxide coatings from the surface of the catalyst. All samples were evaluated at 3 different feed compositions : 1) rich feed, $\lambda = 0.75-0.80$, 2) stoichiometric feed, $\lambda = 1$, and 3) lean feed, $\lambda = 1.15-1.20$.

RESULTS

The results are presented as plots of conversion versus reactor temperature, hereafter referred to as lightoff plots. Within this paper, the lightoff temperature is considered the temperature at which 50 percent conversion occurs. The extent of conversion depends on the stoichiometry of the feed stream. All results presented are lightoff plots comparing the performance of the four catalysts tested at one stoichiometry. Methanol conversion is presented at rich, stoichiometric, and lean conditions, while the stoichiometric cases are presented for the other exhaust components; formaldehyde, carbon monoxide, and propylene.

Methanol Conversion

Methanol conversion under rich conditions is indicated as a function of temperature in Figure 3.a. For the palladium-alumina catalyst, conversion increased to approximately 0.2 at 150 °C, then decreased as the temperature increased to 200 °C. At that point, methanol conversion increased dramatically, achieving greater than 0.8 conversion at 250 °C. The addition of cerium led to a substantial decrease in lightoff temperature, and eliminated the low temperature peak in conversion. With cerium present, conversion increased steadily over the temperature range 120 to 200 °C. With barium in place of cerium, a similar effect was noticed, however, the lightoff temperature was shifted nearly 80 °C to higher temperatures compared to Pd on bare alumina. The addition of cerium to the barium containing catalyst had essentially no effect on the lightoff behavior for methanol.

Similar results were observed for stoichiometric feed conditions. As illustrated in Figure 3.b, the palladium-alumina catalyst exhibited slight conversion at approximately 140 °C, prior to increasing sharply at 200 °C. The addition of cerium provided a small decrease in the observed lightoff temperature to 190 °C and again eliminated the low temperature peak in conversion. In this case, the presence of barium increased the low temperature conversion to 0.2 at approximately 140 °C, but increased the lightoff temperature relative to the Pd-alumina

catalyst. Cerium addition to the barium-containing catalyst eliminated the low temperature conversion and decreased the lightoff temperature to approximately 175 °C.

Results for the lean case, indicated in Figure 3.c, illustrate a narrowing of the lightoff temperature range between the four catalysts. The palladium-alumina catalyst displayed a steady increase in conversion to 0.40 as the temperature increased to 190 °C; the low temperature peak phenomenon was not evident in this case. The addition of cerium did not dramatically affect the lightoff temperature, however, the low temperature conversion was diminished compared to the palladium-alumina case. The addition of barium increased the lightoff temperature by approximately 25 °C relative to all other catalysts, and gave the poorest conversion at low temperature. The addition of cerium to the barium-containing catalyst improved the low temperature conversion from 0.05 at approximately 150 °C for the barium-only case to 0.2 for the combined catalyst. In addition, the combined catalyst provided a lower lightoff temperature by about 20 °C than the barium catalyst.

Comparison of methanol conversion as a function of stoichiometry indicates: 1) Under rich conditions, the catalysts containing cerium or cerium and barium exhibited the lowest lightoff temperatures for methanol, 2) In all three cases the barium catalyst gave the highest lightoff temperature, and 3) The combined cerium-barium catalyst exhibited the lowest lightoff temperature under stoichiometric and lean conditions.

Other Exhaust Components

Formaldehyde conversion under stoichiometric conditions is presented as a function of temperature in Figure 4. For the palladium-alumina catalyst, a steady increase in conversion was observed over the temperature range 100-180 °C, followed by a sharper increase to 0.8 conversion at approximately 225 °C. The cerium catalyst exhibited the low temperature conversion peak observed previously with the palladium-alumina catalyst during methanol conversion, yet provided a lightoff temperature that was essentially the same as the alumina catalyst. The barium catalyst again exhibited the

poorest performance, exhibiting lightoff at approximately 250 °C, or 30 °C higher than the other catalysts. Cerium addition to the barium-containing catalyst lowered the lightoff temperature to approximately the same as the palladium-alumina and the cerium catalysts. Formaldehyde conversion did not exceed 90 percent for any of the catalysts.

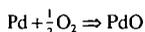
Carbon monoxide (CO) conversion under stoichiometric conditions, shown in Figure 5, was very similar over all four catalysts. Also, the lightoff temperature remained approximately constant between 210 °C and 240 °C, regardless of washcoat composition. Lightoff for CO was much more rapid than was previously noted for methanol, with CO going from near 0% conversion to near 100% conversion in approximately 20 °C. Under stoichiometric conditions complete CO conversion was observed in all catalysts. The combined cerium-barium catalyst yielded the highest lightoff temperature, approximately 25 °C higher than the other catalysts, which all exhibited essentially the same lightoff behavior.

Propylene conversion (Figure 6) displayed many of the same patterns as did the conversion of CO. For this component, as well as CO, the lightoff range narrowed as oxygen content increased. Lightoff temperatures also consistently decreased with increasing oxygen. Propylene exhibited a very narrow temperature range for lightoff, similar to that observed for CO. Conversion increased from essentially 0% to approximately 100% in about 20 °C. Again, the combined cerium-barium catalyst exhibited the highest lightoff temperature of the four catalysts, with 0.5 conversion occurring at approximately 250 °C, as opposed to approximately 220 °C for the palladium-alumina catalyst.

DISCUSSION

The low temperature conversion peak can be interpreted according to previous theory put forth by McCabe, et. al. (1988), for oxidation of formaldehyde over palladium catalyst. In that analysis, it is assumed that the palladium surface is in a reduced state at low temperature conditions but in the oxidized state at higher temperatures. Kinetic analysis of methanol

oxidation over a palladium monolith catalyst has been performed previously (Brewer, and Abraham, 1991) that would seem to support this theory. It may be that the reaction



occurs between 140 and 150 °C. The lower activity of the oxidized surface for oxidation reactions would possibly explain the decrease in catalyst activity in this temperature range. Another explanation could be the presence of two pathways, similar to the mechanism illustrated in Figure 1, where one pathway is favored over a select temperature range and upon passage to sufficiently high temperature a shift back to the major pathway occurs.

The barium catalyst gave the worst performance for methanol oxidation under all conditions. Conversely, catalysts containing cerium consistently were amongst the best-performing catalysts for methanol oxidation. In general, for all catalysts tested in these experiments, an effect of increasing the oxygen concentration was to decrease the lightoff temperature (the exceptions being the lightoff temperatures of 160 °C and 190 °C observed for the cerium-barium and the cerium catalyst under stoichiometric conditions). These observations suggest that cerium enhances the availability of oxygen for the methanol oxidation reaction, whereas barium decreases oxygen availability. As oxygen concentration in the feed increased, and thus its availability for reaction, the influence of cerium was diminished; the inhibition by barium was apparently secondary relative to the enhancement due to cerium.

CONCLUSIONS

Methanol conversion is one of the major topics of concern in methanol-fueled vehicle emissions. Conversions under rich conditions are of particular interest because the vehicles run under rich conditions when they are first started, which is also when catalyst temperatures are low. The cerium catalyst and the combined cerium-barium catalyst displayed the best performance in the conversion of methanol under

rich conditions, the combined Ce-Ba catalyst was best under stoichiometric conditions, and all four catalysts were roughly equal under lean conditions. The barium catalyst generally provided the highest lightoff temperatures of the catalysts tested, although barium did not seem to hinder the performance of the combined cerium-barium catalyst appreciably.

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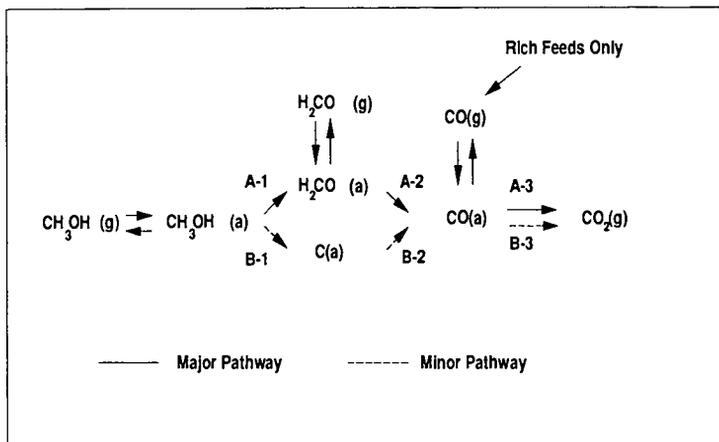


Figure 1: Proposed methanol oxidation pathways (McCabe, et al., 1986). Pathways are simplified. Only carbon-containing species are shown; (a) denotes adsorbed species.

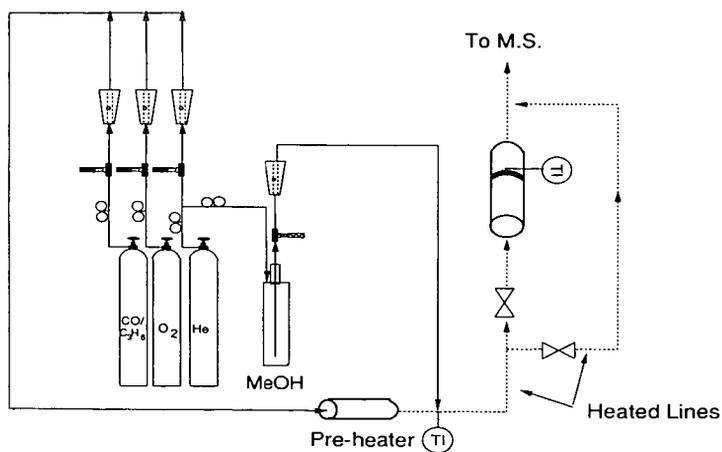


Figure 2: Detailed schematic of experimental apparatus.

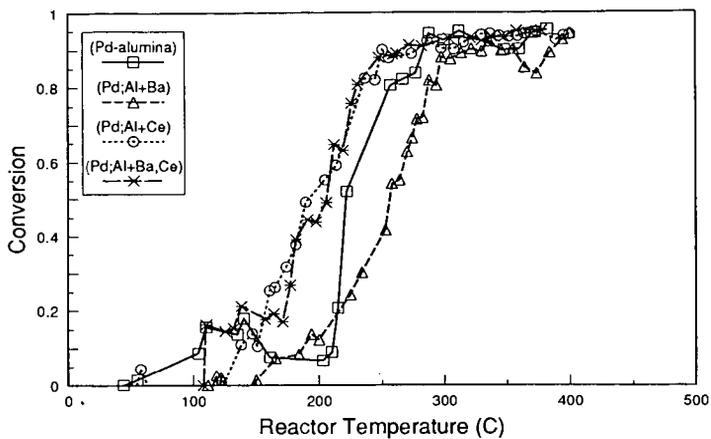


Figure 3.a: Effect of base metal additives on methanol conversion under rich feed conditions ($\lambda < 1$).

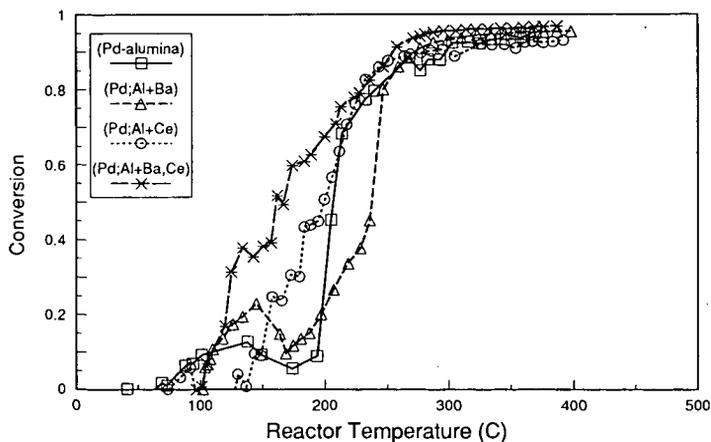


Figure 3.b: Effect of base metal additives on methanol conversion under stoichiometric feed conditions ($\lambda = 1$).

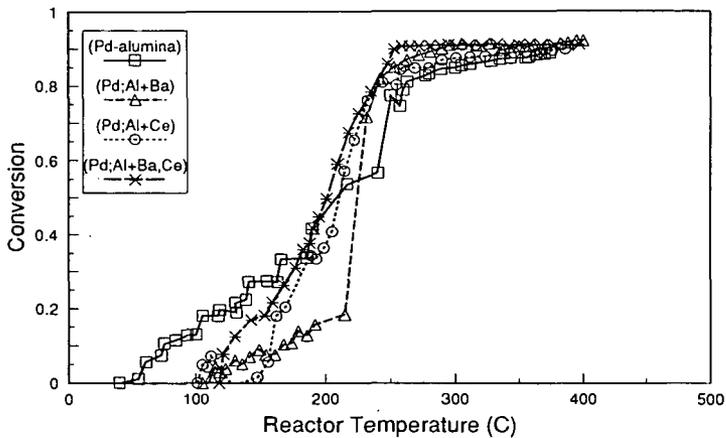


Figure 3.c: Effect of base metal additives on methanol conversion under lean feed conditions ($\lambda > 1$).

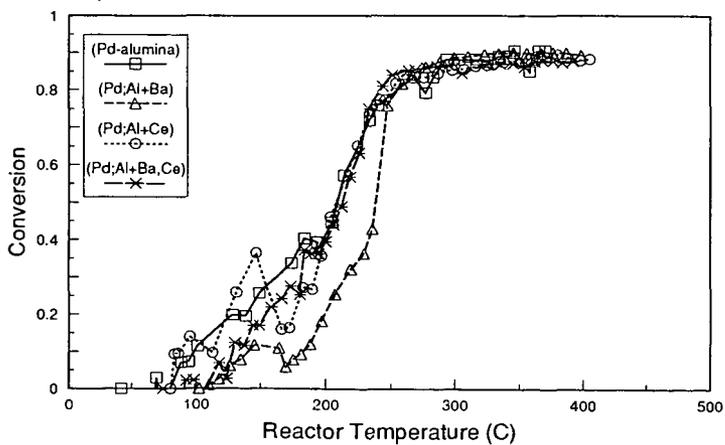


Figure 4: Effect of base metal additives on formaldehyde conversion under stoichiometric feed conditions ($\lambda = 1$).

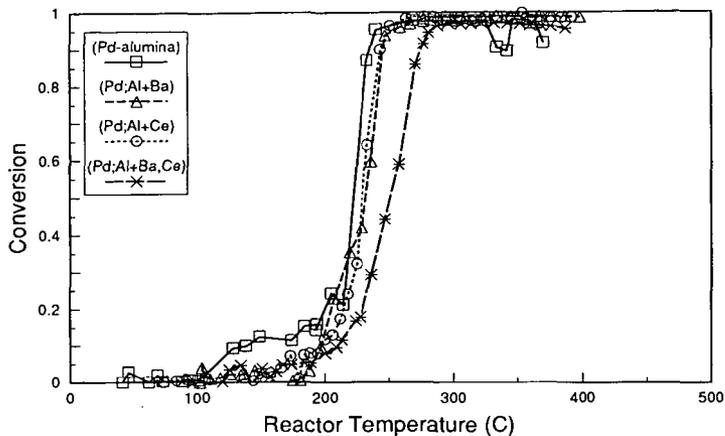


Figure 5: Effect of base metal additives on carbon monoxide conversion under stoichiometric conditions ($\lambda=1$).

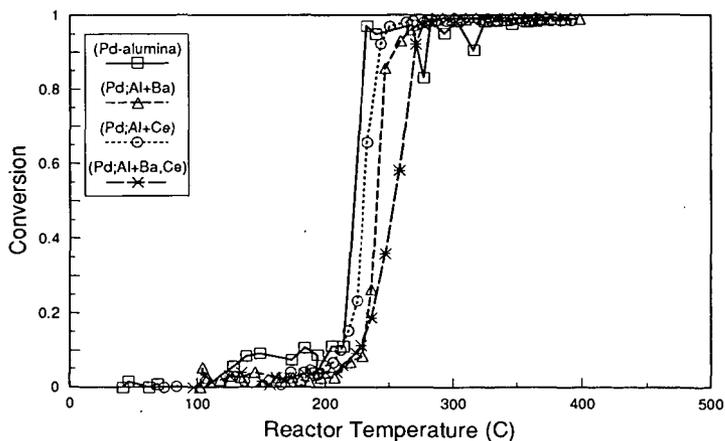


Figure 6: Effect of base metal additives on propylene conversion under stoichiometric conditions ($\lambda=1$).