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Methane Oxidation over Alumina-Supported Noble Metal Catalysts with and without Cerium Additives

SE H. OH,* PATRICIA J. MITCHELL,* AND ROBERT M. SIEWERT†

*Physical Chemistry Department and †Thermosciences Department, General Motors Research Laboratories, Warren, Michigan 48090

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Laboratory reactor experiments have been conducted to evaluate alumina-supported noble metal catalysts, both in the presence and absence of cerium additives, for their effectiveness in the catalytic oxidation of methane under conditions likely to be encountered in natural-gas vehicle exhaust. Under oxidizing conditions, all of the catalysts promoted the complete oxidation of methane to CO_2 and H_2O, with the methane oxidation activity ranking given by Pd > Rh > Pt in the absence of Ce and by Rh > Pd ≈ Pt in the presence of Ce. Under reducing conditions, methane oxidation produced substantial amounts of CO and H_2 as the principal partial oxidation products. In the absence of Ce, the methane oxidation activity decreases in the order Pd > Rh > Pt, with the tendency to form CO decreasing in the order Rh > Pd > Pt. The activity ranking for methane conversion in reducing feedstreams was not affected by the presence of Ce; however, the addition of Ce to the Pt/Al_2O_3 and Pd/Al_2O_3 catalysts almost completely suppressed the formation of the partial oxidation product CO. At a fixed temperature of ~550°C, the methane conversion over each of the noble metal catalysts goes through a maximum as the feedstream concentration of O_2 is varied. The data suggest that O_2 inhibits the CH_4 oxidation under oxidizing conditions by excluding the more weakly adsorbed species, CH_4, from the active sites. Also, methane oxidation experiments in the presence of CO in the feed showed that the methane conversion characteristics of the noble metal catalysts are little affected by the CO.

INTRODUCTION

In recent years natural gas has received increased attention as an alternative fuel for motor vehicles because of its potential technical, economic, and environmental advantages. Natural gas, which consists primarily of methane, has excellent knock resistance and ignition capability over a wide range of air–fuel ratios (*1*). These properties permit natural-gas engines to operate at high compression ratios and with very fuel-lean mixtures, resulting in substantially higher fuel efficiencies than are possible with gasoline engines. Also, natural gas is less expensive than gasoline on an energy basis and is expected to be available well into the next century (*2*). Environmental benefits of natural gas include extremely low photochemical reactivity (*3*), reduced cold-start CO emissions (*1*), and zero evaporative emissions. Furthermore, the low carbon content of methane would lead to reduced CO_2 emissions (the most common "greenhouse" gas) from natural-gas vehicles. However, methane itself is a much more powerful greenhouse gas than CO_2 (*4, 5*) and thus, although not currently regulated, exhaust emissions of unburned methane from natural-gas vehicles are anticipated to be of particular concern in the future.

Vehicle emission tests conducted at General Motors Research Laboratories with two different gasoline engines converted to operate on natural gas (*6*) showed that poor methane conversion (<15% during FTP) occurs over commercial three-way catalysts currently used for gasoline-vehicle exhaust emission control. These dual-fuel vehicles were designed to operate open-loop (lean) when running on compressed natural gas. This observation of low methane conversion

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in the lean natural-gas engine exhaust is not surprising in view of previous reports in the literature (Ref. (*7*) and references therein), which generally show that methane is the most difficult hydrocarbon to oxidize catalytically. The results of these vehicle emission tests also indicate that the optimal catalyst formulation for natural-gas vehicles may differ from that for gasoline vehicles.

This laboratory reactor study was initiated to investigate the possibility of controlling methane emissions by catalytic oxidation of unburned methane present in natural-gas engine exhaust. Most of the previous laboratory studies on the catalytic oxidation of methane [e.g., Refs. (*7–11*)] focused on experimental conditions where there is an excess of oxygen over methane (i.e., $O_2/CH_4 > 2$). Because of the wide ignition range of natural gas, however, actual natural gas engines can potentially be operated under a variety of air–fuel ratio conditions. The currently favored operating strategies for natural-gas engines include fuel-lean and stoichiometric combustion (*1*). Since catalytic activity is often a sensitive function of the stoichiometry of the reaction environment (*12*), it is entirely possible that methane conversion efficiency in natural-gas engine exhaust may vary substantially with the air–fuel ratio. With this possibility in mind, we conducted laboratory methane oxidation experiments with single-component noble metal catalysts over wide ranges of temperatures and feedstream stoichiometries. The results of such laboratory experiments are of practical interest because (1) methane is the principal hydrocarbon species in natural-gas engine exhaust, (2) its oxidation characteristics have not been examined under conditions likely to be encountered in natural-gas vehicle exhaust, and (3) noble metals are ranked among the most active catalysts for methane oxidation (*7, 8*).

EXPERIMENTAL

Catalysts

Two sets of Pt, Pd, and Rh catalysts were used in this study: one supported on spheres of γ-alumina (3 mm diameter, 96 m^2/g BET area) and the other on spheres of Ce-modified alumina (6 wt% Ce uniformly distributed, 3.4 mm diameter, 125 m^2/g BET area). All of the catalysts were prepared by incipient wetness impregnation with aqueous solutions of the metal salts. The metal loadings, metal salts used in the preparation, and CO/metal and H/metal ratios determined from static chemisorption measurements are listed in Table 1. After impregnation, the catalysts were dried in air overnight at room temperature and then calcined in flowing air at 500°C for 4 h. Such procedures resulted in the deposition of the noble metals near the periphery of the catalyst beads. The observation of a CO/Rh atomic ratio in excess of unity for Rh/Al_2O_3 indicates that at least part of the Rh exists as isolated atoms or ions, forming a dicarbonyl species during CO chemisorption (*13, 14*).

Reactor System and Analytical Methods

The integral flow reactor system used in this study was similar to that employed in a previous study (*15*). The reactor was a 2.5-cm-o.d. stainless-steel tube housed in an electric furnace. The feed gases were passed downward through layers of silicon carbide particles and the catalyst pellets. The silicon carbide layer located upstream of the catalyst bed serves as an inert heat transfer medium and also helps establish fully developed flow in the reactive section. Temperatures were measured with a chromel–alumel thermocouple positioned along the reactor centerline with its tip located a few millimeters below the top of the catalyst bed. All the experiments reported here were performed using 15 cm^3 of catalyst and a total feedstream flow rate of 13 liter/min (STP), yielding a space velocity of 52,000 h^{-1}. The feedstream contained 0.2 vol% CH_4, 0.1 vol% CO if present, and variable levels of O_2 in a He background.

The gas stream entering and leaving the reactor was analyzed using a Varian 6000 gas chromatograph equipped with a thermal conductivity detector. A single column

TABLE 1

Catalyst Properties

Catalyst	Metal loading (wt%)	Noble metal precursor	Chemisorption	
			CO/M	H/M
Pt/Al_2O_3	0.20 Pt	H_2PtCl_6	0.60	0.70
Pd/Al_2O_3	0.16 Pd	$PdCl_2$	0.21	0.32
Rh/Al_2O_3	0.14 Rh	$RhCl_3$	1.25	0.42
$Pt/Ce/Al_2O_3$	0.19 Pt, 6 Ce	H_2PtCl_6	0.74	0.81
$Pd/Ce/Al_2O_3$	0.14 Pd, 6 Ce	$PdCl_2$	0.33	0.22
$Rh/Ce/Al_2O_3$	0.13 Rh, 6 Ce	$RhCl_3$	0.95	0.58

(0.32-cm diameter by 1.5-m length) containing molecular sieve 5A was employed, and the chromatographic separations were carried out isothermally at 60°C in a He carrier gas. Individual species in the reaction mixture were identified and quantified by comparing their elution times and integrated areas with those of commercially supplied calibration gases.

The methane oxidation activity of the catalysts was characterized in two ways: (1) temperature run-up experiments with fixed feed composition and (2) variable composition experiments at a fixed temperature. Assessing catalyst behavior using an integral reactor is fraught with uncertainties, especially when highly exothermic reactions such as methane oxidation are occurring in the system. Temperature and concentration gradients, both in the axial and radial directions, can be quite large at high reactant conversions. (The adiabatic temperature rises are 62 and 53°C with and without CO in the feed, respectively.) Furthermore, temperatures and concentrations within the bed are dependent upon the catalytic activity of the sample being tested, and thus it is difficult to control or even characterize the reaction environment of the catalyst very precisely. However, since our primary interest here is in evaluating catalysts for potential automotive application, we chose to measure catalyst performance under carefully controlled *inlet* conditions to the catalyst bed. The reactor temperature was controlled by a thermocouple placed at the outside surface of the reactor tube. However, temperature values quoted in this study (referred to as catalyst temperature) are those actually measured just below the top of the catalyst bed.

RESULTS

Oxidation Activity of Noble Metal Catalysts in CH_4–CO–O_2 Mixtures

Although our principal focus is on the catalytic oxidation of methane, we first conducted laboratory reactor evaluations of the three noble metals Pt, Pd, and Rh in feedstreams that contained CO in addition to methane and O_2. Carbon monoxide, which is present in natural-gas vehicle exhaust in significant quantities (*6*), has been shown to significantly affect the oxidation activity of noble metal catalysts for some hydrocarbons (*16–18*). Furthermore, the presence of CO in the feedstream allows one to examine the conversion efficiencies of both methane and CO simultaneously.

Figure 1 shows the steady-state conversions of CH_4 and CO as a function of temperature for the Pt/Al_2O_3, Pd/Al_2O_3, and Rh/Al_2O_3 catalysts. The experiments were conducted in an oxidizing feedstream containing 0.2 vol% CH_4, 0.1 vol% CO, and 1 vol% O_2. The CO conversion over the Pt/Al_2O_3 and Pd/Al_2O_3 catalysts is near 100% at temperatures as low as ~200°C; however, the Rh/Al_2O_3 catalyst was observed to be much less active for CO oxidation in this

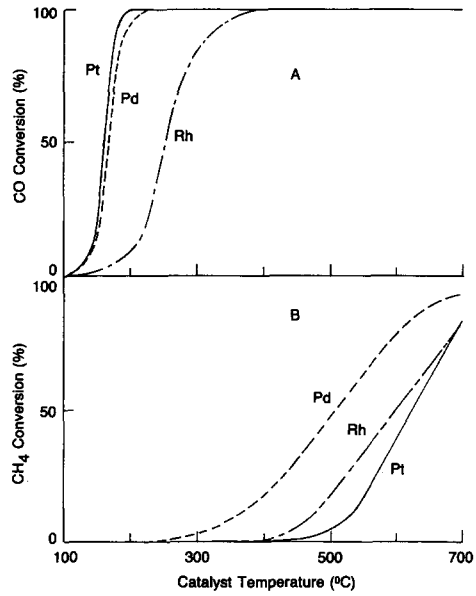

FIG. 1. Conversions of CO (A) and CH_4 (B) over the alumina-supported noble metal catalysts as a function of temperature in an oxidizing feedstream containing 0.2 vol% CH_4, 0.1 vol% CO, and 1 vol% O_2.

oxidizing environment, requiring ~350°C for complete CO conversion.

In agreement with earlier literature reports of extremely low methane oxidation rates (*10, 11, 19*), high temperatures in excess of 500°C are required for 50% conversion of the methane over the noble metals in the oxidizing feedstream employed in Fig. 1. The low reactivity of CH_4 toward O_2 is also reflected in the absence of catalyst lightoff during the methane oxidation. The methane oxidation activity in the presence of excess O_2 decreases in the order Pd/Al_2O_3 > Rh/Al_2O_3 > Pt/Al_2O_3, and this activity ranking is consistent with the observations of Firth and Holland (*9*) and of Yu Yao (*10*). In the oxidizing feedstream of Fig. 1, carbon dioxide was the only carbon-containing reaction product detected at temperatures above 200°C (where the CO in the feed was completely converted), indicating the complete oxidation of the methane in the feed. Complete oxidation of methane was also observed in CO-free oxidizing feeds, as discussed later in this paper.

Since the exhaust composition of actual natural-gas vehicles can fluctuate to the fuel-rich as well as the fuel-lean side of the stoichiometric point, it is of practical interest to examine the performance of the noble metal catalysts under net-reducing conditions. Figure 2 shows steady-state CH_4 and CO conversions as a function of temperature in a reducing feedstream containing 0.2 vol% CH_4, 0.1 vol% CO, and 0.33 vol% O_2. All three noble metals exhibit very similar low-temperature CO oxidation activity, reaching nearly 100% CO conversion at temperatures as low as 200°C. However, the CO conversion efficiencies over the noble metal catalysts begin to fall below 100% near 450°C and then continue to decline with a further increase in temperature. For each of the noble metal catalysts, the temperature required for the onset of the CH_4 oxidation in the reducing feedstream of Fig. 2 is similar

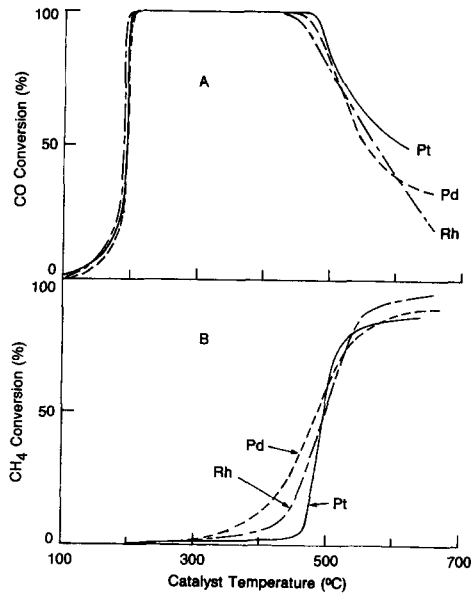

FIG. 2. Conversions of CO (A) and CH_4 (B) over the alumina-supported noble metal catalysts as a function of temperature in a reducing feedstream containing 0.2 vol% CH_4, 0.1 vol% CO, and 0.33 vol% O_2.

to that observed in Fig. 1 for the oxidizing feedstream. Note, however, that once the reaction began, the CH_4 conversion increased much more sharply with temperature (leveling off between 80 and 95% for $T > 550$°C) in the reducing feedstream than it does in the oxidizing feedstream. The observation that the decrease in CO conversion is generally accompanied by an increase in CH_4 conversion in Fig. 2 strongly suggests that the loss in CO conversion efficiency at elevated temperatures is due primarily to partial oxidation of methane to CO under the oxygen-deficient conditions. In fact, our experiments with CH_4–O_2 mixtures (i.e., no CO in the feed) under reducing conditions confirmed the formation of CO as the principal carbon-containing partial oxidation product of methane oxidation. This aspect is discussed later in the paper.

Comparison of Figs. 1B and 2B shows that at temperatures above 500°C the CH_4 conversion over each of the noble metal catalysts is higher in the reducing environment than it is in the oxidizing environment. This suggests the possibility that the CH_4 conversion may be sensitive to the stoichiometry of the gas-phase environment and thus there may exist an optimum feedstream stoichiometry at which a maximum CH_4 conversion occurs. To explore this possibility, we measured steady-state CH_4 and CO conversions at a catalyst temperature of ~550°C using feedstreams containing 0.2 vol% CH_4, 0.1 vol% CO, and variable levels of O_2. A wide range of feedstream stoichiometries was covered by increasing the O_2 concentration step-by-step while holding the temperature and total flow rate constant. The results of such experiments are shown in Fig. 3, where the CH_4 and CO conversions are plotted against the O_2 concentration in the feed. It can be seen in Fig. 3B that for each of the noble metal catalysts, the CH_4 conversion goes through a maximum at an O_2 concentration somewhat less than its stoichiometric value of 0.45 vol% (i.e., in a net-reducing feed) and then declines sharply as the O_2 concentration is increased further. The optimum inlet oxygen concentration for Pt/Al_2O_3 and Rh/Al_2O_3 lies between 0.40 and 0.42 vol% O_2; however, a maximum CH_4 conversion over Pd/Al_2O_3 was observed at a lower inlet O_2 concentration of ~0.35 vol%. The CO conversions measured during the same experiments are plotted in Fig. 3A. For all three noble metal catalysts, the CO conversion increases monotonically with increasing O_2 concentration in the feed, reaching an asymptotic level of 100% at an O_2 concentration between 0.45 and 0.5 vol%. Under reducing conditions, the CO conversion efficiency decreases in the order Pt/Al_2O_3 > Pd/Al_2O_3 > Rh/Al_2O_3.

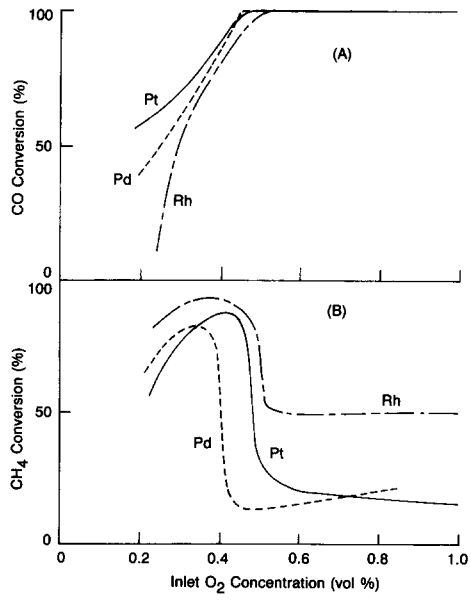

FIG. 3. Conversions of CO (A) and CH_4 (B) over the alumina-supported noble metal catalysts at a catalyst temperature of 550°C in feedstreams containing 0.2 vol% CH_4, 0.1 vol% CO, and variable levels of O_2.

Oxidation Activity of Noble Metal Catalysts in CH_4–O_2 Mixtures

Additional methane oxidation experiments were carried out over the same alumina-supported noble metal catalysts without CO in the feed. Comparison of the

results of these experiments with those presented in the previous section allows one to examine how the CH_4 converison characteristics of the noble metal catalysts are affected by the presence of CO in the feed. Also, experiments under conditions where CO is absent in the reactant gas mixture provide useful insight into the origin of the CO observed during our previous methane oxidation experiments in a reducing environment and the tendencies of the various noble metals to partially oxidize methane to CO.

Temperature run-up experiments conducted in an oxidizing CH_4–O_2 feedstream (0.2 vol% CH_4, 1 vol% O_2, no CO) revealed methane conversion characteristics similar to those depicted in Fig. 1B. Although not shown, the methane oxidation over each of the noble metal catalysts in the absence of CO began at a temperature comparable to that required for the CO-containing oxidizing feed of Fig. 1. As was also observed in Fig. 1B, the onset of the reaction was followed by a gradual increase in methane conversion with temperature (i.e., absence of catalyst lightoff), although the conversion over Pd/Al_2O_3 and Rh/Al_2O_3 was somewhat more sensitive to temperature in the absence of CO than in the presence of CO. Furthermore, in agreement with the results of Fig. 1B, the methane oxidation activity in the CO-free oxidizing feed was found to decrease in the order $Pd/Al_2O_3 > Rh/Al_2O_3 > Pt/Al_2O_3$, forming CO_2 as the only carbon-containing reaction product (i.e., complete oxidation of methane). The observation that the CH_4 conversion characteristics during a temperature run-up are essentially unaffected by CO in the feed is not surprising in view of the large disparity in their reactivity toward O_2. That is, much higher temperatures are required for methane oxidation than for CO oxidation, so that all the CO has been completely reacted by the time the CH_4 conversion becomes significant (see Fig. 1).

Similarly, the methane conversion vs temperature data over the noble metal catalysts under reducing conditions were also little affected by the presence of CO in the feed. Temperature run-up experiments with a reducing feedstream containing 0.2 vol% CH_4, 0.33 vol% O_2, and no CO yielded methane conversion data similar to those shown in Fig. 2B. The similarities in methane oxidation features between the cases with and without CO include (1) the onset of methane oxidation at a comparable temperature for each of the noble metals, (2) the same activity ranking ($Pd/Al_2O_3 > Rh/Al_2O_3 > Pt/Al_2O_3$) for low methane conversions, and (3) similar asymptotic methane conversion levels of ~90% for temperatures above 550°C. Again, the insensitivity of CH_4 conversion to the added CO under reducing conditions can be attributed to complete CO conversion at temperatures where the CH_4 begins to react (see Fig. 2).

Although added CO does not directly affect CH_4 conversion characteristics on either side of the stoichiometric point, it consumes oxygen in the feed and consequently changes the value of the critical inlet O_2 concentration at which an abrupt decline in methane conversion occurs. This aspect becomes apparent when the methane conversion vs O_2 concentration data of Fig. 3B (in the presence of CO) are compared with those of Fig. 4 (in the absence of CO). In both cases the catalyst temperature was set

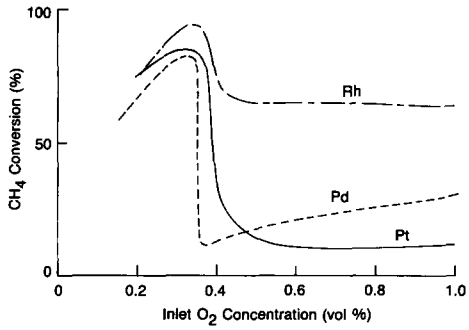

FIG. 4. CH_4 conversion over the alumina-supported noble metal catalysts at a catalyst temperature of 550°C in feedstreams containing 0.2 vol% CH_4 and variable levels of O_2.

TABLE 2

Product Distributions for Methane Oxidation Under Reducing Conditions[a]

Catalysts	CH_4 Consumed (ppm)	CO_2 Produced (ppm)	CO Produced (ppm)	H_2 Produced (ppm)
Pt/Al_2O_3	1005	820	163	600
Pd/Al_2O_3	1000	800	250	715
Rh/Al_2O_3	1560	1025	560	2700

[a] 0.2 vol% CH_4 and 0.15 vol% O_2 in the feed, catalyst temperature = ~520°C, space velocity = 52 000 h^{-1}.

at ~550°C and the feedstream concentration of CH_4 was held constant at 0.2 vol%. It is evident that an increase in the inlet O_2 concentration affects the CH_4 conversion in identical fashion regardless of whether or not CO is present in the feed. The only significant difference between Figs. 3B and 4 is that for each of the noble metals, a precipitous drop in CH_4 conversion occurs at a lower O_2 concentration in the absence of CO than it does in the presence of CO in the feed. Such a shift of the methane conversion curves toward lower O_2 concentrations in the CO-free feed of Fig. 4 is related to the fact that the stoichiometric amount of O_2 decreases from 0.45 to 0.40 vol% as 0.1 vol% CO is removed from the reactant stream.

For all three noble metal catalysts, methane oxidation under reducing conditions produced CO and H_2 as the principal products of partial oxidation. Our observation of H_2 as a reaction product during methane oxidation is perhaps not surprising in view of the report of Frennet (*20*) that at elevated temperatures methane chemisorption on noble metals is accompanied by H_2 evolution. Experiments conducted with feedstreams containing no CO were particularly convenient in examining the product distributions and the tendencies of the various noble metal catalysts to form CO during methane oxidation. Table 2 shows the amounts of CO, CO_2, and H_2 produced and the amount of CH_4 consumed during methane oxidation under reducing conditions (0.2 vol% CH_4, 0.15 vol% O_2, and no CO in the feed) over the three noble metal catalysts at a catalyst temperature of ~520°C. For each of the noble metal catalysts, there is a good correlation between the amount of CH_4 reacted and the sum of the amounts of CO and CO_2 produced during the methane oxidation (carbon balance closure to within 5%), indicating that CO and CO_2 are the only carbon-containing reaction products under our experimental conditions. (The presence of elemental carbon on the surface is ruled out because O_2 exposure of the catalyst following steady-state reaction at low O_2/CH_4 ratios did not produce significant amounts of CO or CO_2.) For all the runs conducted under reducing conditions, including those presented in Table 2, the mass balance for oxygen agreed within 10% when CO, CO_2, H_2, and H_2O were assumed to be the only reaction products. Considering the uncertainty associated with the H_2 analysis (typical precision = ±5% of the reported value; our GC column was not optimized for H_2 analysis), it appears that no partial oxidation products other than CO and H_2 are formed in significant quantities under our reaction conditions. Although trace amounts of methanol, formaldehyde, and formic acid have also been reported as the reaction products in some cases (*21*), we did not pursue this point in detail.

The product selectivity to CO (i.e., the amount of CO produced divided by the amount of CH_4 consumed) for each noble metal can be calculated from the data of Table 2: 0.16 for Pt/Al_2O_3, 0.25 for Pd/Al_2O_3, and 0.36 for Rh/Al_2O_3. These calculated selectivities indicate that the ten-

dency to form the partial oxidation product CO decreases in the order Rh/Al_2O_3 > Pd/Al_2O_3 > Pt/Al_2O_3, in agreement with the ranking of the noble metal catalysts for CO conversion observed under the reducing feedstream conditions of Fig. 3. It is interesting to note that the H_2/CO ratio differs significantly among the noble metals: ~4 for Pt/Al_2O_3, ~3 for Pd/Al_2O_3, and ~5 for Rh/Al_2O_3. These compare with a H_2/CO ratio of 2 expected for the dissociative adsorption of methane leading to the cleavage of the C–H bond, a key step in methane oxidation over noble metals (*7, 10, 11*). This implies that for all three noble metals, the CO generated during the methane oxidation reacts more readily with oxygen than the H_2. In fact, the high H_2/CO ratio observed for the Rh/Al_2O_3 catalyst is consistent with the results of separate reactor experiments with $CO–H_2–O_2$ mixtures (*22*), which show that Rh/Al_2O_3 is particularly effective in preferentially oxidizing CO in the presence of a large excess of H_2.

Oxidation Activity of Ceria-Promoted Noble Metal Catalysts in $CH_4–CO–O_2$ Mixtures

Since cerium is the most common base metal additive for commercial three-way catalyst formulations, it is of practical interest to examine how the activity and selectivity of the noble metal catalysts for methane oxidation are affected by the presence of Ce. Figure 5 shows the steady-state conversions of CH_4 and CO over the $Pt/Ce/Al_2O_3$, $Pd/Ce/Al_2O_3$, and $Rh/Ce/Al_2O_3$ catalysts as a function of temperature in an oxidizing feedstream containing 0.2 vol% CH_4, 0.1 vol% CO, and 1 vol% O_2. It can be seen that the CO conversion characteristics under oxidizing conditions are similar with and without Ce; that is, as observed in Fig. 1A with the Ce-free noble metal catalysts, the CO in the feed was completely reacted over $Pt/Ce/Al_2O_3$ and $Pd/Ce/Al_2O_3$ at temperatures as low as ~220°C while a substantially higher temperature (~320°C) was required for complete CO conversion over $Rh/Ce/Al_2O_3$. In contrast, comparison of Figs. 1B and 5B shows that the CH_4 oxidation activity of Pt/Al_2O_3 and Pd/Al_2O_3 under oxidizing conditions is retarded markedly in the presence of Ce. The activity of the Rh/Al_2O_3 catalysts for CH_4 oxidation was observed to be little affected by Ce, however. The Ce-induced suppression of the CH_4 oxidation activity was observed to be most dramatic for Pd/Al_2O_3 (~200°C increase in the 50% conversion temperature); consequently, the activity ranking in the presence of excess O_2 changes from Pd > Rh > Pt without Ce (Fig. 1B) to Rh > Pd ≈ Pt with Ce (Fig. 5B). A similar detrimental effect of Ce addition was reported for the oxidation of other saturated hydrocarbons (such as $n–C_4H_{10}$) over Pt/Al_2O_3 and Pd/Al_2O_3 (*10*). Under the strongly oxidizing conditions of Fig. 5, all the Ce-containing noble metal catalysts promoted the complete oxidation of CH_4 to CO_2 and H_2O.

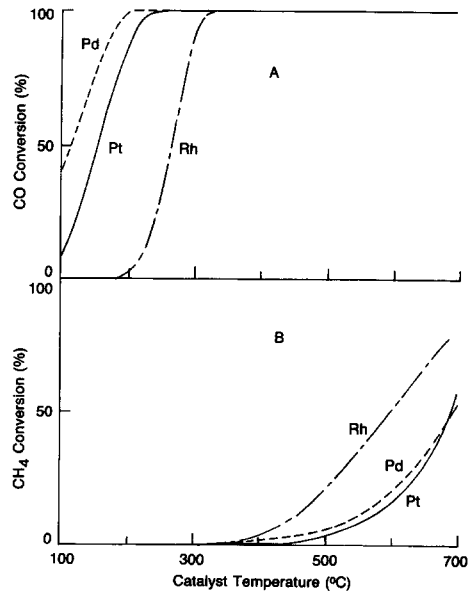

FIG. 5. Conversions of CO (A) and CH_4 (B) over the ceria-promoted alumina-supported noble metal catalysts as a function of temperature in an oxidizing feedstream containing 0.2 vol% CH_4, 0.1 vol% CO, and 1 vol% O_2.

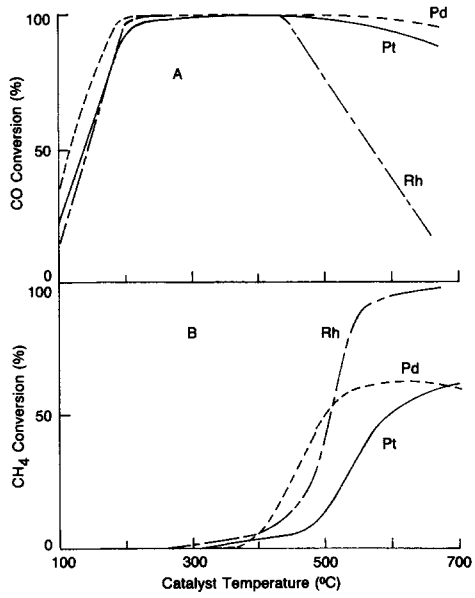

FIG. 6. Conversions of CO (A) and CH_4 (B) over the ceria-promoted alumina-supported noble metal catalysts as a function of temperature in a reducing feedstream containing 0.2 vol% CH_4, 0.1 vol% CO, and 0.33 vol% O_2.

Shown in Fig. 6 are the results of temperature run-up experiments with the Ce-containing noble metal catalysts in a reducing feedstream containing 0.2 vol% CH_4, 0.1 vol% CO, and 0.33 vol% O_2. All three Ce-containing noble metal catalysts exhibit similar low-temperature CO oxidation activity, achieving nearly complete CO conversion at ~220°C. The CO conversion over $Pt/Ce/Al_2O_3$ and $Pd/Ce/Al_2O_3$ remained high (>90%) as the temperature was increased up to 650°C. Over the $Rh/Ce/Al_2O_3$ catalyst, on the other hand, complete CO conversion was maintained only up to ~450°C; the CO conversion declined gradually with a further increase in temperature (to a 20% level at 650°C). Comparison of Figs. 2B and 6B reveals that for each of the noble metals, the temperature required for the onset of the CH_4 reaction in the reducing feedstream is little affected by the presence of cerium in the catalysts. Note, however, that the CH_4 conversion levels reached at elevated temperatures over $Pt/Ce/Al_2O_3$ and $Pd/Ce/Al_2O_3$ (~65%) are substantially lower than those over the Ce-free counterparts (85–90%). The lower CH_4 conversion levels observed at high temperatures for the Ce-containing Pt/Al_2O_3 and Pd/Al_2O_3 catalysts appear to be a direct consequence of their tendency to promote the total oxidation of CH_4. In this high-temperature, oxygen-deficient regime, the CH_4 conversion would likely be limited by the oxygen availability and thus a lower CH_4 conversion is expected for the total oxidation of CH_4 than for the partial oxidation. In fact, assuming 100% conversion of the CO in the feed and the total oxidation of methane, the highest possible CH_4 conversion at the 0.33 vol% inlet O_2 level is calculated to be 70%, in close agreement with the maximum conversion of ~65% observed in Fig. 6B for $Pt/Ce/Al_2O_3$ and $Pd/Ce/Al_2O_3$. In contrast, the presence of Ce in the Rh/Al_2O_3 catalyst did not significantly alter the CH_4 conversion at high temperatures; just as we saw with the Ce-free Rh/Al_2O_3 catalyst (Fig. 2B), the CH_4 conversion over $Rh/Ce/Al_2O_3$ approached 100% in the high-temperature regime, but only at the expense of decreased CO conversion. Thus, under the reducing conditions of Fig. 6, the activity and product selectivity of Rh/Al_2O_3 for CH_4 oxidation are virtually unaffected by the presence of Ce, whereas the addition of Ce to Pt/Al_2O_3 and Pd/Al_2O_3 suppresses the formation of the partial oxidation product CO (with the concomitant decrease in CH_4 conversion at elevated temperatures).

Another aspect of cerium's contribution to the performance of the noble metal catalysts during methane oxidation at ~550°C is depicted in Fig. 7. Recall that over the Ce-free noble metal catalysts (Fig. 3B), the CH_4 conversion goes through a maximum as the inlet O_2 concentration is increased before the conversion drops precipitously near the stoichiometric O_2 concentration of 0.45 vol%. The Ce-containing Pd/Al_2O_3 and Rh/Al_2O_3 catalysts (Fig. 7B) show the same behavior; that is, the CH_4 conversion declines

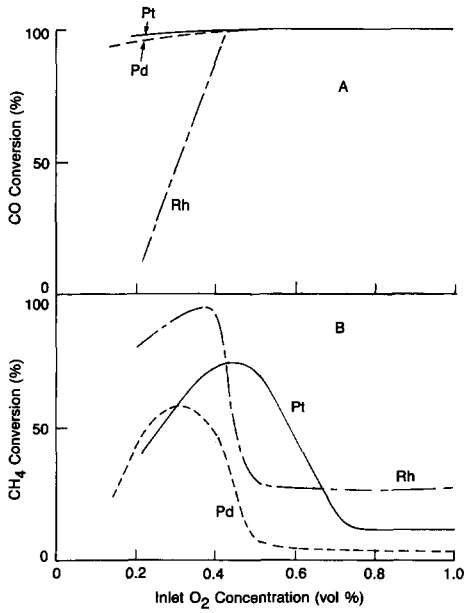

FIG. 7. Conversions of CO (A) and CH_4 (B) over the ceria-promoted alumina-supported noble metal catalysts at a catalyst temperature of 550°C in feedstreams containing 0.2 vol% CH_4, 0.1 vol% CO, and variable levels of O_2.

sharply when a near-stoichiometric amount of O_2 (0.4 to 0.5 vol%) is present in the feed. It is important to note, however, that the Pt/Ce/Al_2O_3 catalyst stands alone in its ability to maintain relatively high CH_4 conversions in a feedstream that contains a considerable excess of O_2. This suggests the possibility of widening the air/fuel ratio "window" in the operation of actual natural-gas vehicles by adding Ce to Pt/Al_2O_3 catalysts.

Figure 7A shows the CO conversion data over the Ce-containing noble metal catalysts obtained during the same variable O_2 concentration experiments discussed above. In accordance with the temperature run-up data of Fig. 6A, the CO conversion over Pt/Ce/Al_2O_3 and Pd/Ce/Al_2O_3 remains high (>95%) throughout the entire O_2 concentration range considered here. This points to the tendency of the Ce-containing Pt/Al_2O_3 and Pd/Al_2O_3 catalysts to oxidize CH_4 to CO_2 (rather than CO) even under extremely oxygen-deficient conditions. Separate experiments with the same Pt/Ce/Al_2O_3 and Pd/Ce/Al_2O_3 catalysts but with feeds containing only CH_4 and O_2 confirmed that the amount of CO produced as a result of partial oxidation of methane was indeed minimal. Unlike the cases with Pt/Ce/Al_2O_3 and Pd/Ce/Al_2O_3, a substantial amount of CO was produced over the Rh/Ce/Al_2O_3 catalyst under the reducing conditions of Fig. 7, where a limited amount of O_2 reacted with a mixture of CH_4 and CO. Rhodium exhibits such a tendency to form CO during methane oxidation regardless of whether or not Ce is present in the catalyst, as evidenced by the close similarity between the CO conversion curves in Figs. 3A and 7A.

Figures 6 and 7 reveal that the high CO conversions achieved over the Pt/Ce/Al_2O_3 and Pd/Ce/Al_2O_3 catalysts under reducing conditions are accompanied by the relatively low CH_4 conversions (compared to those for their Ce-free counterparts shown in Figs. 2 and 3). This indicates that as Ce is added to Pt/Al_2O_3 and Pd/Al_2O_3, the increased CO conversion under reducing conditions is offset to some degree by the loss in CH_4 conversion efficiency. The appropriate trade-offs for practical emission control are beyond the scope of this laboratory study.

DISCUSSION

Reaction Mechanism for Methane Oxidation

Under the oxidizing feedstream conditions considered here, the noble metal surface is predominantly covered with oxygen and thus the critical step in the methane oxidation is the dissociative adsorption (and subsequent reaction) of CH_4 onto the oxygen-covered surface (*10, 11, 23–25*). The supporting evidence for this conclusion is given below. First, most kinetic studies conducted over noble metal catalysts in the presence of excess O_2 show that the observed rate law is first order in methane and zero order in oxygen (*11, 19, 24*). Second, oxygen adsorption on noble metals is fast under the reaction conditions considered here (*26*), whereas methane adsorption is a

slow, activated process (*20*). As a result of the substantial difference in adsorption strengths ($O_2 > CH_4$), O_2 inhibits the CH_4 oxidation under oxidizing conditions by excluding the more weakly adsorbed species, CH_4, from the active sites, as observed in Figs. 3B, 4, and 7B. (The presence of CO in the feed would probably not significantly change the relative surface concentration of CH_4 and O_2 under reaction conditions, because CO tends to desorb rapidly from the surface at the high temperatures required for the methane reaction.) As the O_2 concentration in the feed is decreased to less than the stoichiometric value (while holding the concentration of the reducing agents constant), however, CH_4 can compete successfully with O_2 for the active sites despite its weaker adsorption strength. In this case, the adsorption rates for both reactants would become comparable, yielding a high reaction rate and thus high CH_4 conversion. With a further decrease in inlet O_2 concentration, insufficient amounts of O_2 adsorb on the surface and the CH_4 conversion becomes low because of the resulting kinetic and/or stoichiometric limitations encountered during the methane oxidation. This explains why the CH_4 conversion goes through a maximum as the inlet O_2 concentration is varied, as illustrated in Figs. 3B, 4, and 7B. A similar dependence of methane conversion on exhaust stoichiometry, including a maximum CH_4 conversion under somewhat richer than stoichiometric conditions, was observed over commercial noble metal catalysts in a recent engine-dynamometer study with methane fuel (*27*).

The detailed mechanism of methane oxidation on noble metals is not yet well understood. Methane chemisorption and methane–deuterium exchange experiments (*20, 28*) have shown that the chemisorption of methane on noble metals involves dissociation to adsorbed methyl or methylene radicals, as a result of removal of hydrogen atoms from the carbon atom. The subsequent interaction of methyl or methylene radicals with adsorbed oxygen has been proposed to lead to either direct oxidation to CO_2 and H_2O or the formation of chemisorbed formaldehyde via methoxide, methyl peroxide, or methylene oxide intermediates (*7, 23, 29, 30*). Recent studies of formaldehyde oxidation on Pt by McCabe and McCready (*31*) and by Lapinski *et al.* (*32*) provided kinetic and spectroscopic evidence that the oxidation reaction involves the dissociation of the adsorbed formaldehyde to adsorbed CO and adsorbed H atoms. These adsorbed CO and H atoms have been observed to either desorb as CO and H_2 or react with adsorbed oxygen to produce CO_2 and H_2O, depending on the stoichiometry of the reactant gas mixture (*31, 32*). Based on the above discussion, the proposed reaction mechanism for methane oxidation can be summarized as

$$\begin{array}{l} CH_4(g) \\ \quad\Updownarrow \\ CH_4(a) \end{array} \xrightarrow{-H} \begin{array}{c} CH_3\cdot(a) \\ \text{or} \\ CH_2\cdot(a) \end{array} \xrightarrow{+O} \begin{array}{l} HCHO(g) \\ \quad\Updownarrow \\ HCHO(a) \end{array} \xrightarrow{\text{decomp.}} \begin{array}{l} CO(g) \quad H_2(g) \\ \quad\Updownarrow \quad\quad\Updownarrow \\ CO(a) + 2H(a) \end{array} \xrightarrow{+O} \begin{array}{l} CO_2(g) \\ + \\ H_2O(g) \end{array}$$

The mechanism proposed above is consistent with our observation of CO, CO_2, H_2, and H_2O as the principal reaction products of the methane oxidation under reducing conditions. Although not directly measured, material balance considerations indicate that no significant amount of gaseous formaldehyde was produced during the methane oxidation over the noble metal catalysts. This suggests that under our reaction conditions an adsorbed formaldehyde intermediate, once formed, may rapidly decompose to CO(a) and H(a) rather than desorb into the gas phase as formaldehyde molecules.

Given the presence of CO, CO_2, H_2, and H_2O in the reaction mixture, it is possible that the product distribution for the methane oxidation may be altered by the water–gas shift equilibrium reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O.$$

TABLE 3

Methane Conversion and CO Production With and Without CO_2 Addition

	Pt/Al_2O_3		Pd/Al_2O_3		Rh/Al_2O_3	
	CH_4 Conv. (%)	CO (ppm)	CH_4 Conv. (%)	CO (ppm)	CH_4 Conv. (%)	CO (ppm)
Base case[a]	50	163	50	250	78	560
1000 ppm CO_2 Added	51	177	52	275	76	687
2000 ppm CO_2 Added	51	181	50	250	76	750

[a] 0.2 vol% CH_4 and 0.15 vol% O_2 in the feed (no CO_2 added), catalyst temperature = ~520°C, space velocity = 52 000 h^{-1}.

The equilibrium constant for the reaction as written above is sufficiently large under our experimental conditions (0.25 at 525°C) so that a significant amount of CO can be formed from the CO_2 and H_2 produced during the methane oxidation. In fact, such a reaction mechanism has recently been proposed by Ashcroft *et al.* (*33*) for selective oxidation of methane to synthesis gas over transition metal catalysts. The importance of the water–gas shift equilibrium to the activity and product selectivity for our methane oxidation experiments was examined by first establishing a steady-state reaction condition at ~520°C with a reducing feedstream containing 0.2 vol% CH_4 and 0.15 vol% O_2 and then adding CO_2 stepwise to the feedstream while holding the temperature and total flow rate constant. This experimental verification is based on the fact that if the shift reaction is operative in our system, the addition of CO_2 to the feed should increase CO production. (Adding CO_2, rather than H_2, is preferable because it allows one to probe the shift reaction without perturbing the feedstream stoichiometry.) The results of such experiments for the three alumina-supported noble metal catalysts are presented in Table 3, which lists methane conversions and the amounts of CO produced during methane oxidation with and without CO_2 addition to the feed. (A more detailed description of the product distribution for the base case is given in Table 2.) It can be seen that for each of the noble metal catalysts the methane conversion is independent of the CO_2 level in the reaction mixture. The amount of CO produced over either Pt/Al_2O_3 or Pd/Al_2O_3 is also virtually unaffected by the CO_2 addition. For the Rh/Al_2O_3 catalyst, on the other hand, increasing the CO_2 level in the reaction mixture tends to enhance CO production (and, although not shown, suppress H_2 production) during the methane oxidation. This suggests that the water–gas shift reaction plays a significant role in determining the product selectivity for methane oxidation over Rh/Al_2O_3, but not over Pt/Al_2O_3 or Pd/Al_2O_3. The insensitivity of the methane conversions over the noble metals to the CO_2 level in the feed suggests that the rate-limiting step in the methane oxidation, which is generally believed to be the dissociation of adsorbed methane molecules (*10, 11*), is unaffected by CO_2.

Effects of Ce Additive on Catalytic Properties

Comparison of Figs. 1B and 5B shows that the methane oxidation activity of Rh/Al_2O_3 under oxidizing conditions is not significantly affected by the presence of Ce. In contrast, the methane conversions over the $Pt/Ce/Al_2O_3$ and $Pd/Ce/Al_2O_3$ catalysts were observed to be considerably lower than those over the Ce-free counterparts. The detrimental effect of Ce addition on the methane oxidation activity is particularly pronounced for Pd; the 50% conversion

temperature increased by nearly 200°C when Ce was added to the Pd/Al_2O_3 catalyst. A similar activity suppression by Ce was also observed for the oxidation of other alkanes (C_3H_8 and C_4H_{10}) over Pd/Al_2O_3 in the presence of excess oxygen (*10, 34*). The low alkane oxidation activities observed over Ce-containing Pd/Al_2O_3 catalysts under oxidizing conditions have been shown to be related to the tendency of the Ce to promote the formation of bulk oxide of palladium (*34*), which is much less active for methane oxidation than the surface oxygen on the palladium crystallites (*24, 35*). A similar metal–ceria interaction has been reported for the $Pt/Ce/Al_2O_3$ system; Summers and Ausen (*36*) and Yu Yao (*10*) presented IR and kinetic evidence to suggest that Ce promotes/stabilizes an oxidized platinum species. Thus, the Ce-induced suppression of the methane oxidation activity over Pt/Al_2O_3 (~70°C increase in the 50% conversion temperature) can be attributed to the Pt being converted into a less active, oxidized state as a result of interaction with the Ce. Ce may interact with Rh in the same way as with Pt or Pd; however, since the oxidation state of the Rh/Al_2O_3 surface changes readily in response to a change in its gaseous environment at temperatures above 200°C (*12, 37*), the extent and stability of Rh oxide formation under our reaction conditions are likely to be dominated by the stoichiometry of the reactant gas mixture rather than by the presence of Ce. This may explain why the Rh/Al_2O_3 catalyst with and without Ce exhibits similar methane oxidation activity in the oxidizing feedstream of Figs. 1 and 5.

The observation that the kinetic behavior of Rh/Al_2O_3 is not affected by Ce carries over to the reducing feedstream conditions employed in Figs. 2 and 6, where the conversions of both CH_4 and CO over Rh/Al_2O_3 were observed to be similar to those over $Rh/Ce/Al_2O_3$. Particularly noteworthy in Fig. 6 is the observation that unlike their Ce-free counterparts, the $Pt/Ce/Al_2O_3$ and $Pd/Ce/Al_2O_3$ catalysts maintain high (>90%) CO conversions even at high temperatures (>450°C) where the methane oxidation becomes significant. This indicates the tendencies of Ce-containing Pt/Al_2O_3 and Pd/Al_2O_3 to produce only minimal amounts of CO during methane oxidation under reducing conditions. The underlying reasons for the suppression of CO formation over $Pt/Ce/Al_2O_3$ and $Pd/Ce/Al_2O_3$ are uncertain. One possible explanation might be that in the presence of Ce, adsorbed CO on the noble metals (generated from partial oxidation of methane) reacts readily with surface oxygen derived from the neighboring ceria particles to produce CO_2 before it desorbs as gaseous CO. In this case, the limited supply of O_2 in the feed would be consumed by the partial oxidation product CO in preference to the CH_4 over the ceria-promoted Pt and Pd catalysts, resulting in relatively low levels of CH_4 conversion under reducing conditions as illustrated in Figs. 6 and 7. In fact, the methane conversion efficiencies observed in Fig. 6B for the Ce-containing Pt and Pd catalysts at high temperatures are close to a maximum methane conversion (70%) expected when assuming that none of the CH_4 in the feed is partially oxidized to CO in the presence of Ce. In contrast to Pt/Al_2O_3 and Pd/Al_2O_3, the CO conversion characteristics of Rh/Al_2O_3 are virtually unaffected by Ce (compare Figs. 2A and 6A). This implies that the nature of metal–ceria interaction in $Rh/Ce/Al_2O_3$ might be different from that in $Pt/Ce/Al_2O_3$ or $Pd/Ce/Al_2O_3$. Also, this difference in CO conversion characteristics among the Ce-containing noble metal catalysts may be related to the fact that the water–gas shift reaction plays a significant role in determining the product selectivity of Rh/Al_2O_3, but not Pt/Al_2O_3 or Pd/Al_2O_3. Further work is required to clarify the role of Ce in modifying the kinetics of methane oxidation over noble metals.

Hysteresis in Methane Oxidation Activity over Pd/Al_2O_3

All the temperature run-up data reported here represent stabilized activities and selectivities measured by carrying out repetitive runs in the feedstream of interest with

the catalyst samples initially calcined in air for 4 h at 500°C. The results of the variable O_2 concentration experiments shown in Figs. 3, 4, and 7 were generated by first heating the sample to the desired temperature (~550°C) in a strongly reducing feedstream and then adding O_2 stepwise to the feed, with the temperature, total flow rate, and CH_4 and CO concentrations held constant. In order to investigate how the catalytic behavior is affected by the sample history, we conducted additional variable O_2 concentration experiments at ~550°C with the Ce-free noble metal catalysts by decreasing the O_2 concentration in the feed step-by-step starting from an oxidized state of the catalyst. For Pt/Al_2O_3 and Rh/Al_2O_3, the results of such experiments were found to be similar to those of the original variable O_2 concentration experiments shown in Figs. 3 and 4, indicating that these two catalysts arrived at essentially the same final steady-state condition regardless of whether they started from a reduced or an oxidized state. However, the oxidation activity of the Pd/Al_2O_3 catalyst is a strong function of its prior history; that is, plots of methane conversion vs O_2 concentration at a catalyst inlet temperature of ~550°C followed drastically different paths depending on the direction of O_2 concentration change, as depicted in Fig. 8 for feedstreams containing 0.2 vol% CH_4, 0.1 vol% CO, and variable levels of O_2. (The CO conversion over Pd/Al_2O_3, on the other hand, was not significantly different.) A transition from the low conversion branch to the high conversion branch in the net-oxidizing regime of Fig. 8 could not be achieved simply by varying the O_2 concentration in the feed. It was found, however, that cooling the reactor to ≤300°C in He followed by a run-up to ~550°C in a strongly oxidizing reactant mixture (e.g., one containing 1 vol% O_2) was effective in restoring the high activity state of the Pd/Al_2O_3 catalyst. This points to the importance of a low-temperature exposure to an oxidizing environment in reactivating the Pd/Al_2O_3 catalyst. Although the detailed

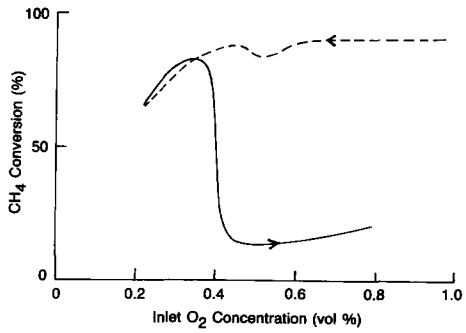

FIG. 8. Effects of the direction of O_2 concentration change on methane conversion over Pd/Al_2O_3 at a catalyst temperature of 550°C in feedstreams containing 0.2 vol% CH_4, 0.1 vol% CO, and variable levels of O_2.

mechanism for the catalyst activation process is not certain at this time, it is likely that the activity enhancement arises from the high reactivity of surface oxygen covering the Pd crystallites, which has been reported to form in an oxidizing environment at low temperatures (*24, 38, 39*). During a high-temperature oxidizing treatment of palladium, on the other hand, the surface oxygen species has been shown to migrate into the bulk, forming unreactive Pd bulk oxide (*24, 38, 39*). This would explain the low methane oxidation activity observed at high O_2 concentrations on the lower branch of Fig. 8. Also, once activated by a low-temperature oxidizing treatment, the oxygen coverage on the Pd surface during methane oxidation may be well below the saturation limit as a result of depletion of surface oxygen by the reaction. Since oxygen penetration into the bulk is generally believed to occur from an oxygen-saturated surface (*38*), it is possible that, once activated in a low-temperature oxidizing environment, the Pd/Al_2O_3 catalyst remains resistant to bulk oxide formation (and thus retains its high activity state, as observed) during the subsequent run-up to 550°C in an oxidizing feedstream. Further work is required to better understand the structure–activity relationship for Pd in general, and to verify the above-mentioned catalyst reactivation mechanism in particular.

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