

# Catalytic Oxidation of Methane over ZrO<sub>2</sub>-Supported Pd Catalysts

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The catalytic oxidation of methane has been examined in an integral reactor over Pd/ZrO<sub>2</sub> catalysts in this study in order to determine how various preparation pretreatment and reaction variables influence activity. The conversion of methane versus temperature data indicate that mild oxidative and reductive treatments enhance the activity of a 5 wt% Pd/ZrO<sub>2</sub> catalyst while a higher-temperature reductive pretreatment produces a less efficient catalyst. Increasing the Pd loading from 0.1 to 10 wt% improves catalytic performance while higher loadings yield negligible improvement. Decay studies were performed on a 5 wt% Pd/ZrO<sub>2</sub> catalyst and compared to those of an optimized Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Under the conditions used in this study, the activity of the Pd/ZrO<sub>2</sub> catalyst remains fairly constant over a 50-hr period while the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst initially exhibits an increase in activity but then a decrease after approximately 16 hr. At 250°C the Pd/ZrO<sub>2</sub> converts 56% of the methane to CO<sub>2</sub> and H<sub>2</sub>O after approximately 45 hr while the Pd/Al<sub>2</sub>O<sub>3</sub> catalytically oxidizes only 32% of the methane under the same conditions. An optimized Pd/ZrO<sub>2</sub> catalyst achieves a methane conversion of 100% below 300°C, which is 40°C lower than that obtained using the optimized Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.

The 5 wt% Pd/ZrO<sub>2</sub> CH<sub>4</sub>-oxidation catalyst also was characterized using X-ray photoelectron spectroscopy before and during heating in vacuum at 180°C and after treatment in a 2:1 mixture of O<sub>2</sub> and CH<sub>4</sub> at 180°C and 100 Torr for 45 min. The near-surface region of the as-entered catalyst consists mostly of ZrO<sub>2</sub> and PdO along with some Pd metal. Some of the PdO is reduced to Pd metal at 180°C, which is near the onset temperature for methane oxidation, and the Pd signal is diminished probably due to agglomeration of the Pd. Exposure of the catalyst to a 100 Torr mixture of 2:1 O<sub>2</sub> and CH<sub>4</sub> at 180°C for 45 min results in the formation of adsorbed CH<sub>x</sub>, CO and CO<sub>3</sub><sup>=</sup> and/or HCO<sub>3</sub><sup>=</sup> species. These data suggest that the CH<sub>4</sub> hydrogen bonds are first broken to form an adsorbed carbon species, which reacts with surface oxygen to form an adsorbed CO. This CO then reacts to form a surface carbonate or bicarbonate species which decomposes to form CO<sub>2</sub>. © 1999 Academic Press

## INTRODUCTION

Natural gas provides an attractive alternative to gasoline as an economic fuel source since it is in abundant supply and will be readily available for decades. The use of natural gas as a fuel also has environmental benefits because its ignition temperature for combustion is lower than that

of gasoline, it contains very low levels of sulfur and nitrogen impurities resulting in reduced NO<sub>x</sub> and SO<sub>x</sub> emissions, and the H-to-C ratio is high, leading to the formation of more water than CO<sub>2</sub>. Natural gas does, however, consist primarily of methane, which is a potent greenhouse gas (1, 2). Therefore, noncombusted methane must be eliminated from the exhaust streams of natural-gas burning engines. This can be accomplished using a catalytic converter containing an appropriate catalyst material. The catalyst must oxidize nearly 100% of the methane in the exhaust stream at temperatures below 400°C and remain active for many years.

Conventional three-way catalytic converters exhibit poor performance for this application (3). This is not surprising because methane is the most difficult hydrocarbon to oxidize catalytically because it contains no C–C bonds so that strong C–H bonds must be broken. Past and present research on the catalytic oxidation of methane has focused primarily on Pd/Al<sub>2</sub>O<sub>3</sub> catalysts (4–12), and these studies have shown that the activity of each catalyst is influenced by many factors including precursor and support materials used, Pd loading, calcination temperature, Pd crystallite morphology, catalyst pretreatment, and reaction conditions. It has been reported that the activity of this catalyst initially increases as a function of time (8, 10). Baldwin and Burch (8) have demonstrated that at a reactor temperature of 267°C, their Pd/Al<sub>2</sub>O<sub>3</sub> catalyst becomes four times more active over a 300-hr time period. The sensitivity of the activity to the structure of the catalyst surface and to the oxidation state of Pd has been examined, and different conclusions have been reached (8, 9, 11). Although most studies on the catalytic oxidation of methane have been performed using alumina as the support, other materials have been tested as well. Titania, thoria, and tin oxide have been used as supports for Pd by Cullis and Willat (5) and were found to be active for methane oxidation but not as active as a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst under identical reaction conditions. Hoflund and co-workers (13) have studied the oxidation of methane over Pd/ZrO<sub>2</sub>, Pd/CeO<sub>2</sub>, and Pd/Mn<sub>3</sub>O<sub>4</sub> catalysts using both nanocrystalline and polycrystalline support materials. Pd-based catalysts supported on nanocrystalline ZrO<sub>2</sub> and CeO<sub>2</sub> supports demonstrate appreciable activities below

300°C under the reaction conditions tested. Zirconia has also been used previously as a support for Pd in catalytic methane oxidation studies by Ribeiro *et al.* (11), Seimanides and Stoukides (14), Marti *et al.* (15), and Carstens *et al.* (16). Ribeiro *et al.* demonstrated that the use of a 10 wt% Pd/ZrO<sub>2</sub> catalyst results in a higher methane oxidation reaction rate than a 0.77 wt% Pd/Si–Al<sub>2</sub>O<sub>3</sub> catalyst. At a reactor operating temperature of 550 K, Pd/ZrO<sub>2</sub> catalysts performed better than all others tested. Recently, Carstens *et al.* (16) examined the factors which affect the catalytic activity of Pd/ZrO<sub>2</sub>, particularly with regard to the chemical state of the Pd. For these reasons a detailed reaction and surface characterization study of the oxidation of methane over Pd/ZrO<sub>2</sub> catalysts has been performed. The effects of Pd loading, calcination temperature, pretreatment, and the methane-to-oxygen feed ratio have been examined, and decay studies have been carried out as well. The decay behavior is compared to that obtained from a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst optimized for methane oxidation (17). This study has been performed using an integral reactor. Since the conversions are typically large, no attempt has been made to extract kinetic parameters in this study. Furthermore, product concentrations (CO<sub>2</sub> and H<sub>2</sub>O) are large at high conversions, which may influence reaction rate.

The active surface species and mechanism for this reaction, however, have not been identified due to difficulties associated with the surface characterization of a catalyst under reaction conditions. The oxidation of CH<sub>4</sub> to H<sub>2</sub>O and CO<sub>2</sub> begins between 150 and 200°C over Pd/ZrO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts (4–7, 9–11, 18). Even without the presence of Pd metal, this reaction occurs on many oxides including ZrO<sub>2</sub> at significant rates below 300°C. Furthermore, Burch and co-workers (19, 20) have shown that Al<sub>2</sub>O<sub>3</sub>-supported Pd metal is not active for the catalytic oxidation of methane. Therefore, the active phase for this catalytic reaction must be the oxide surfaces, and improvements in rate due to the addition of metals such as Pd may occur through an enhanced dissociative chemisorption rate for methane followed by spillover onto the oxide support and/or the presence of Pd oxides. This view supports the assertion that dissociative chemisorption of methane is the rate-limiting step in the overall reaction.

In order to gain a better understanding of the reaction process, the surface of the 5 wt% Pd/ZrO<sub>2</sub> catalyst has been characterized in this study using X-ray photoelectron spectroscopy (XPS) after insertion into an ultrahigh vacuum (UHV) chamber, while heating at 180°C in the UHV chamber and after exposure to a 1:2 CH<sub>4</sub> and O<sub>2</sub> mixture for 45 min at 100 Torr and 180°C.

## EXPERIMENTAL

The Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/ZrO<sub>2</sub> samples were prepared from a Pd(NO<sub>3</sub>)<sub>2</sub> precursor (99.9% pure on a metals basis) pur-

chased from Alfa AESAR. The Al<sub>2</sub>O<sub>3</sub> support (99.97% purity) also was purchased from Alfa AESAR, and the ZrO<sub>2</sub> support (99% purity) was purchased from Aldrich Chemical Co. The catalysts were prepared by mixing the precursor and support in distilled water and then stirring while heating to remove the excess water. The remaining slurry was calcined in air at 110, 280, 500, or 800°C for 2 hr. Then 100 mg of each catalyst was tested in a tubular quartz reactor by passing a feed stream consisting of 0.8% CH<sub>4</sub>, 9.6% O<sub>2</sub>, and 89.6% N<sub>2</sub> through the catalyst bed at a flow rate of 31 cm<sup>3</sup>/min and a total pressure of 16 psig. All feed gases were of research-grade purity and were well mixed before entering the reactor. In order to determine the activity at each temperature, the catalyst bed temperature was held constant, within ±3°C, until a maximum in activity was obtained. During the decay studies, the reactor was operated at 200, 250, and 300°C, and the product-stream analysis was performed at various time intervals using a Hewlett–Packard Series 5790A gas chromatograph which had been calibrated using an Alltech standard consisting of 1% H<sub>2</sub>, 1% CH<sub>4</sub>, 1% CO<sub>2</sub>, and 97% N<sub>2</sub>. A Tenax column purchased from Alltech was used to separate these gas components.

For the surface studies a 5 wt% Pd/ZrO<sub>2</sub> catalyst sample was pressed into an Al cup, inserted into the UHV chamber, and characterized using XPS. XPS was performed using a double-pass cylindrical mirror analyzer (DPCMA) (PHI Model 25-255AR) and pulse counting detection (21) by operating the DPCMA in the retarding mode using a pass energy of 25 eV for the high-resolution spectra and 50 eV for the survey spectra. The X rays were generated using a MgK $\alpha$  X-ray source. After characterization the Pd/ZrO<sub>2</sub> catalyst was radiatively heated to 180°C in vacuum using a tungsten filament positioned beneath the sample holder and characterized again at this temperature. The catalyst sample was then moved into an attached chamber and heated to 180°C under 100 Torr of a 1:2 CH<sub>4</sub> and O<sub>2</sub> mixture for 45 min. After this treatment the sample was characterized again without exposure to air.

## RESULTS AND DISCUSSION

### Reaction Studies

The Pd/ZrO<sub>2</sub> catalysts prepared and tested in this study have an average BET surface area of 24.5 m<sup>2</sup>/g with a variation of ±2 m<sup>2</sup>/g. For most metal-supported catalysts, the metal is catalytically active while the oxide support is not. These Pd/ZrO<sub>2</sub> catalysts are unusual because the bare ZrO<sub>2</sub> is an active catalyst for methane oxidation (13, 18), whereas supported Pd metal is inactive (19, 20). Furthermore, as described below, both the Pd chemical state and structure change with treatment. Baldwin and Burch (8) have shown that based on these facts the total surface area given by the

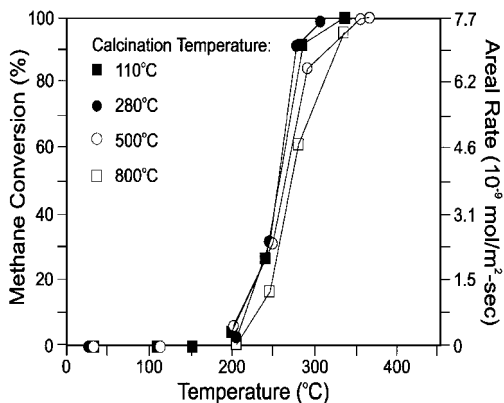


FIG. 1. Influence of calcination temperature on the conversion of methane as a function of reactor operating temperature using a 5 wt% Pd/ZrO<sub>2</sub> catalyst.

BET measurements and not the Pd dispersion is the more appropriate variable to use to characterize the catalytic activity of these materials. Since so many factors influence the performance of methane oxidation catalysts, comparison of dissimilar catalysts is difficult.

The influence of calcination temperature on the activity of a 5 wt% Pd/ZrO<sub>2</sub> catalyst as a function of reactor operating temperature is shown in Fig. 1. Conversion of methane to CO<sub>2</sub> and H<sub>2</sub>O begins for each catalyst somewhat below 200°C except in the case of the catalyst calcined at 800°C, which exhibits the worst performance of those tested. Typically, calcination treatments above 400°C are performed to dry, oxidize, and thermally stabilize the catalyst material. Under the reaction conditions examined in the present study, the samples prepared using the lower calcination temperatures of 110 and 280°C catalyze the oxidation reaction more effectively than those calcined at higher temperatures. This may be due to the fact that surface hydroxyl groups remain after calcining at the lower temperatures, that the Pd or Pd-oxide crystallites do not sinter to form larger particles, or that the structures formed at lower calcining temperatures are more catalytically active. Hicks *et al.* (9) attribute differences in the catalytic activity of similar catalysts to Pd particle size and oxidation state differences, while Baldwin and Burch (8) argue that structure is more important. The catalyst calcined at 280°C exhibits the best performance at reaction temperatures above 250°C. At 200°C the catalyst calcined at 500°C has a slightly larger activity than the others, but the conversions attained using the catalysts calcined at the lower temperatures are similar. As discussed below, the surface hydroxyl groups are believed to participate in the reaction. Calcination at the higher temperature most likely eliminates many hydroxyl groups through desorption of water which would result in reduced catalytic activity. The catalyst calcined at 280°C was tested three times in sequence; i.e., the temperature versus conversion data were collected through three cycles

using the same catalyst. The deviations in the conversions between each cycle were within  $\pm 1.7\%$ . The differences in conversion in Fig. 1 at temperatures near 200°C are close to this error range. Since these conversions are small, they may be more susceptible to various types of experimental error.

In most studies presented in the literature, Pd/Al<sub>2</sub>O<sub>3</sub> catalysts were calcined at elevated temperatures (400–600°C) and then reduced in H<sub>2</sub> (300–500°C). The effects of mild reductive and oxidative pretreatments on the activity of a 5 wt% Pd/ZrO<sub>2</sub> catalyst calcined at 500°C have been examined and are shown in Fig. 2. For comparison, the data obtained from an as-prepared Pd/ZrO<sub>2</sub> catalyst with no pretreatment also are shown in Fig. 2. The reductive treatment was performed using a 1 : 8 mixture of H<sub>2</sub> and N<sub>2</sub>, and the oxidative treatment was performed using a 1 : 8 mixture of O<sub>2</sub> and N<sub>2</sub> both flowing at 31 cm<sup>3</sup>/min. The catalyst reduced at 250°C attains a conversion above 10% at 200°C, whereas the catalyst which was reduced at 400°C does not achieve this conversion below 250°C. At this same temperature the catalyst given the milder pretreatment attains a conversion of almost 40%. The catalyst treated in oxygen at 250°C performs similarly to the catalyst reduced at 250°C except at the lower operating temperature of 200°C, where the oxygen-treated catalyst performs slightly worse than the catalyst reduced at 250°C but better than the as-prepared catalyst. The assumption is typically made that a reductive treatment reduces the surface by eliminating surface oxygen. However, in a previous study of TiO<sub>2</sub>(001) (22), Hoffund and co-workers have demonstrated that the surface becomes enriched in oxygen under reductive conditions. Similar oxygen enrichments have been observed in studies of Zn/Cr, higher alcohol synthesis catalysts after heating in a reductive environment (23). This enrichment is due to migration of sub-surface oxygen to the surface through a chemically induced driving potential produced by the reductive treatment.

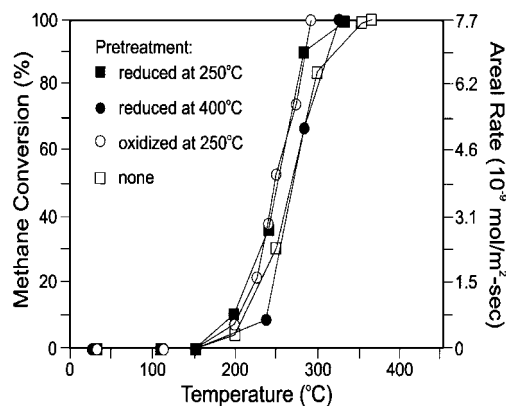


FIG. 2. Influence of pretreatment conditions on the conversion of methane as a function of reactor operating temperature using a 5 wt% Pd/ZrO<sub>2</sub> catalyst calcined at 500°C for 2 hr.

In a study of oxygen-exposed, polycrystalline Pd (24), a hydrogen treatment has been found to induce migration of subsurface oxygen to the outermost atomic layer. Based on the data in Fig. 2, the 250°C reductive treatment may produce a surface which is chemically similar to that obtained by heating the catalyst in oxygen at 250°C, which would explain their similar catalytic behaviors. These surfaces may be enriched in surface oxygen or in some form of reactive oxygen species. The performance of the catalyst reduced at 400°C is similar to that of the as-prepared catalyst. Reductive pretreatments at elevated temperatures (>250°C) have been shown to enhance the activity of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts toward methane oxidation while oxidative treatments lower the catalyst activity (5, 25). Baldwin and Burch (6, 7) postulated that this is due to reconstruction of the Pd crystallites to larger sizes and/or changes in the reactivity of the surface oxygen (6, 26, 27). Apparently, Pd/ZrO<sub>2</sub> catalysts behave in a different manner. This may be due to the lower surface area of the ZrO<sub>2</sub> resulting in larger Pd or Pd-oxide crystallites for a given loading which are less likely to reconstruct. However, the Pd may become more oxidized during both the mild (250°C) oxidative and reductive pretreatments, thereby increasing the reactivity of the surface oxygen.

The influence of Pd loading on catalyst performance is shown in Fig. 3, and the temperatures at which these catalysts yield 50% conversion of the feed methane ( $T_{1/2}$ ), calculated using linear interpolation, are listed in Table 1. Each of these catalysts was calcined at 280°C and tested without further pretreatment. Since the BET surface areas are fairly low, these loadings correspond to high Pd loadings per cm<sup>2</sup>. The catalyst containing the smallest Pd loading of 0.1 wt% has a  $T_{1/2}$  of 338°C, which is only about 12°C lower than that of bare ZrO<sub>2</sub>. This temperature decreases monotonically to 234°C as the Pd loading is increased to 10 wt%. The activity profile and  $T_{1/2}$  value of the 20 wt% Pd/ZrO<sub>2</sub>

TABLE 1

Temperature at Which Each Pd/ZrO<sub>2</sub> Catalyst Achieves a Conversion of 50%

Pd (wt%)	$T_{1/2}$ (°C)
0.0	350
0.1	338
0.5	284
2.0	270
5.0	253
10.0	234
20.0	233

Note. Each catalyst was calcined at 280°C.

catalyst are very similar to those of the 10 wt% Pd/ZrO<sub>2</sub> catalyst, indicating that the activity reaches a maximum at a Pd loading of about 10 wt%. According to the data shown in Fig. 3, the catalysts with higher Pd loadings also perform better at lower temperatures. Bare polycrystalline zirconia powder is active for CH<sub>4</sub> oxidation, as shown in Fig. 3, but the addition of Pd enhances its activity. The onset of activity is near 150°C for the catalysts with the higher Pd loadings, whereas it is closer to 200°C for the bare support. Like Pd/Al<sub>2</sub>O<sub>3</sub> the reaction over Pd/ZrO<sub>2</sub> is limited by the activation barrier for methane dissociation on the Pd. At high Pd loadings the rate of increase in the conversion of methane is larger than at low loadings due to the availability of more reactive Pd sites for methane dissociation. This does not, however, mean that the activity per unit of metal surface area increases also. In fact, at higher Pd loadings on Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, a decrease in the activity per unit of Pd surface area has been observed (5). Under the reaction conditions used in this study, 100% conversion can be achieved below 300°C, as shown in both Figs. 2 and 3. An optimized Pd/Al<sub>2</sub>O<sub>3</sub> catalyst requires a higher temperature to achieve a 100% conversion under identical reaction conditions (17).

The influence on conversion of varying the O<sub>2</sub>:CH<sub>4</sub> feed ratio from oxygen-lean to oxygen-rich conditions over a 5 wt% Pd/ZrO<sub>2</sub> catalyst (calcined at 280°C and not pretreated) at 250°C is shown in Fig. 4. The initial volumetric ratio of O<sub>2</sub>:CH<sub>4</sub> was 5:1. As the amount of O<sub>2</sub> in the feed stream is decreased relative to the amount of CH<sub>4</sub>, the conversion of methane to CO<sub>2</sub> and H<sub>2</sub>O decreases. Below the stoichiometric ratio of 2:1, the amount of feed methane was increased while the amount of oxygen in the feedstream was held constant, and the conversion decreases more sharply attaining a value of approximately 34% at an O<sub>2</sub>:CH<sub>4</sub> feed ratio of 1:4. The reason for the sustained activity is that the ZrO<sub>2</sub> support material acts as an oxygen reservoir. As the amount of oxygen in the zirconia is depleted, the conversion decreases. Studies on Pd/Al<sub>2</sub>O<sub>3</sub> have shown that CO and H<sub>2</sub> form under O<sub>2</sub>-lean conditions at elevated temperatures where the full consumption of oxygen occurs (27-29).

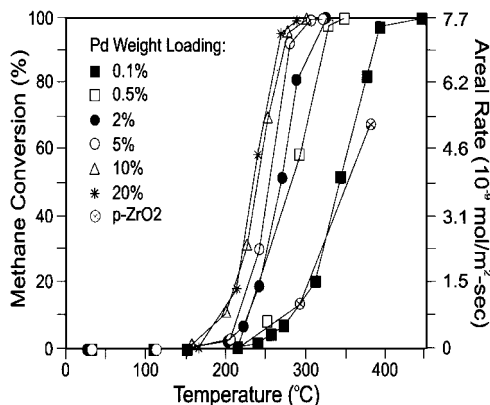


FIG. 3. Influence of Pd loading on the conversion of methane as a function of reactor operating temperature. These catalysts were calcined at 280°C and tested without further pretreatment.

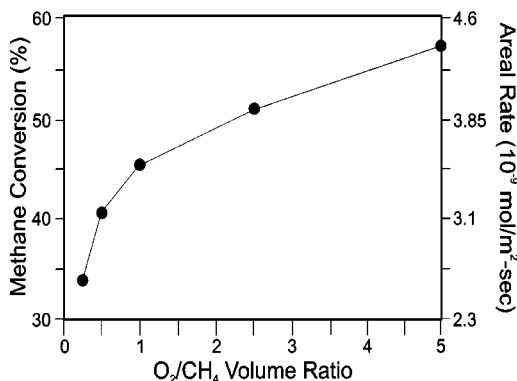


FIG. 4. Influence of the  $O_2:CH_4$  volumetric feed ratio on the conversion of methane using a 5 wt% Pd/ZrO<sub>2</sub> catalyst at 250°C. These catalysts were calcined at 280°C and tested without further pretreatment.

The experiments in this present study were not run at conversions corresponding to complete oxygen consumption at stoichiometric or substoichiometric ratios so CO and H<sub>2</sub> are not formed.

The utilization of a catalyst in an industrial application or in a catalytic converter requires an appreciable catalyst lifetime with minimal decay in activity. Therefore, a 5 wt% Pd/ZrO<sub>2</sub> catalyst was tested to determine the activity as a function of time at constant temperatures of 200, 250, and 300°C, and the results are shown in Fig. 5. At 200°C the conversion is initially 10% and then quickly drops to about 5%. No changes are apparent over the next 250 min. At 250°C the conversion is almost 60%, and it essentially remains constant for more than 8000 min. At 300°C, a constant conversion of about 97% is obtained for 170 min with no indication of decay. In order to compare the performance of this catalyst to Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, an optimized Pd/Al<sub>2</sub>O<sub>3</sub> catalyst (17) was examined under identical reaction conditions at 250°C. The same amount of Pd was present on

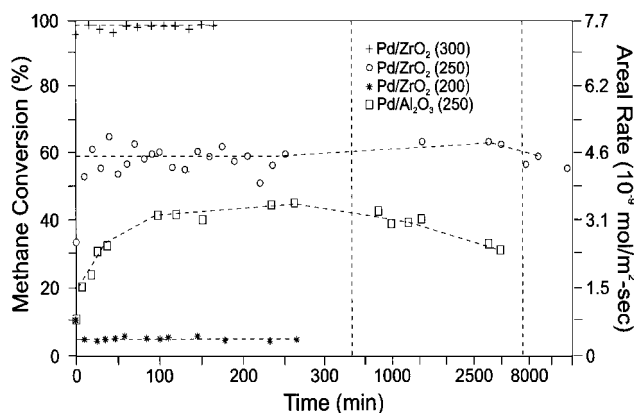


FIG. 5. Methane conversion as a function of time for a 5 wt% Pd/ZrO<sub>2</sub> catalyst at 200, 250, and 300°C and an optimized 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst at 250°C. In all cases the catalyst was calcined at 280°C.

both Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/ZrO<sub>2</sub> catalysts tested. Its activity increases from 15 to 40% over the initial 150 min of testing and then remains nearly constant for the next 450 min. However, after approximately 2600 min the activity of the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst decreases to about 33% and continues to decrease to 31% at 2900 min. These results are not in complete agreement with those presented in other studies (8, 10), where a continual increase in activity was noted over many hours. This may be due to differences in reaction conditions and/or the catalysts. It should be noted that the methane conversions reported in this study are greater than those reported previously (8), indicating that the catalysts tested are different in some respect.

### Surface Characterization Studies

An XPS survey spectrum obtained from the as-prepared 5 wt% Pd/ZrO<sub>2</sub> catalyst is shown in Fig. 6. Features due to Pd, Zr, and O as well as carbon-containing contamination are evident. The carbon contamination may have adsorbed either during the catalyst preparation or during the air exposure prior to insertion into the UHV system. The Pd 3d and Zr 3p features have similar binding energy (BE) values and are therefore difficult to distinguish in this spectrum. A high-resolution Pd 3d and Zr 3p spectrum obtained from the as-prepared catalyst is shown in Fig. 7a. It contains distinct Pd and Zr features which correspond to the presence of PdO and ZrO<sub>2</sub>. A shoulder due to metallic Pd is also present, and a small amount of PdO<sub>2</sub> may be present. The Zr 3d spectrum shown in Fig. 8a obtained from the as-prepared catalyst indicates that the only state of Zr in the near-surface region in significant quantities is ZrO<sub>2</sub> (30). This sample was then heated to 180°C, about the temperature where the onset of reaction occurs, in the UHV system and held at this temperature for 45 min. An

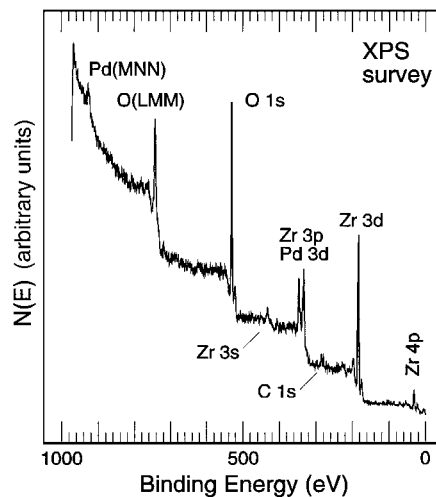


FIG. 6. XPS survey spectrum obtained from an as-prepared 5 wt% Pd/ZrO<sub>2</sub> methane oxidation catalyst.

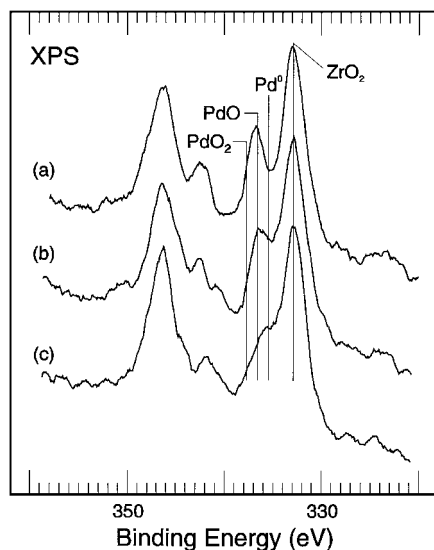


FIG. 7. High-resolution XPS Pd 3d spectra obtained from (a) the as-received 5 wt% Pd/ZrO<sub>2</sub> catalyst, (b) the catalyst while heating at 180°C for 45 min in the UHV chamber, and (c) the catalyst after exposure to 100 Torr of a 1 : 2 CH<sub>4</sub> and O<sub>2</sub> mixture at 180°C for 45 min.

XPS Zr 3d spectrum obtained with the sample held at 180°C is shown in Fig. 8b. No differences are observable compared to the spectrum in Fig. 8a, indicating that the near-surface region of the ZrO<sub>2</sub> support material is not affected by this reductive annealing treatment. The corresponding XPS Pd 3d spectrum, shown in Fig. 7b, contains an enhanced signal contribution due to the presence of Pd metal relative to the PdO feature. Bulk PdO powder does not reduce to Pd

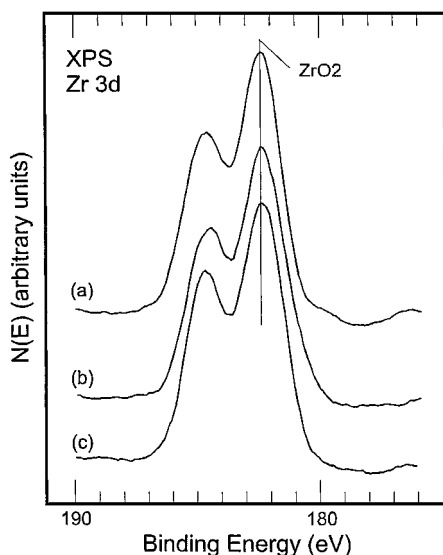


FIG. 8. High-resolution XPS Zr 3d spectra obtained from (a) the as-received 5 wt% Pd/ZrO<sub>2</sub> catalyst, (b) the catalyst after heating at 180°C for 45 min in the UHV chamber, and (c) the catalyst after exposure to 100 Torr of a 1 : 2 CH<sub>4</sub> and O<sub>2</sub> mixture at 180°C for 45 min.

metal at these low temperatures (31), and supported PdO particles are not reduced to Pd metal in the presence of oxygen below 870°C (32). Furthermore, Voogt *et al.* (33) have demonstrated that after heating for 50 min at 773 K in vacuum, a 50-Å-thick PdO layer on a polycrystalline Pd foil is decreased only to 40 Å in thickness. However, XPS studies performed on Pd-containing automotive catalysts have shown that multiple states of Pd can exist on a support and that one of these states is easily reducible to Pd metal at room temperature in H<sub>2</sub> (34, 35). The catalyst examined in this present study was heated in a reductive UHV environment and under typical methane oxidation reaction conditions in an excess of O<sub>2</sub>. Both treatments result in the conversion of PdO to Pd metal. The presence of Pd metal sites allows for dissociative adsorption of CH<sub>4</sub> (35) to compete with O<sub>2</sub> adsorption. Since catalytic oxidation of methane does not occur over supported Pd metal (19, 20), there must be spillover of the dissociated methane fragments onto the support surface or to Pd-oxide regions where they are oxidized. This may partially explain why smaller Pd crystallites are preferred. Compared to the bare ZrO<sub>2</sub> support, the presence of Pd metal provides more sites for dissociation of methane, which allows the overall reaction to proceed more rapidly. Another possibility is that the close proximity of Pd metal and PdO results in an increased reaction rate because the methane dissociates on the Pd metal sites and is oxidized by PdO. However, this may not be significant since the support plays an important role and is a far better catalyst itself than Pd metal, which most likely is partially oxidized. An electronic interaction between the support and the Pd which influences the catalytic behavior is consistent with the observed behavior. The XPS data presented here provide evidence that these Pd metal sites are present on the support material at the temperatures where the reaction begins. Furthermore, as the temperature is increased, the concentration of Pd metal sites increases resulting in more rapid adsorption of CH<sub>4</sub> and increased reaction rate compared to bare zirconia.

This catalyst sample was transferred to an attached reaction chamber and exposed to a 1 : 2 mixture of CH<sub>4</sub> and O<sub>2</sub> at 180°C and 100 Torr for 45 min and then transferred back to the UHV analysis chamber without air exposure and characterized with XPS. An XPS Zr 3d spectrum obtained from this sample is shown in Fig. 8c. Again no changes are observable in the Zr features, indicating that the ZrO<sub>2</sub> support material remains unchanged by this treatment. Other Zr species may be present at the surface but in such small concentrations that they are not apparent in the XPS spectra. Zr metal has a BE value of approximately 178.7 eV (30), which differs by about 3 eV from the BE of ZrO<sub>2</sub>. No contribution to the signal is apparent at or near 178.7 eV, indicating that Zr metal is not produced in measurable quantities during any of these treatments. The XPS Pd 3d and Zr 3p high-resolution spectrum taken from the catalyst treated in the

reaction mixture is shown in Fig. 7c. The Pd  $3d_{5/2}$  feature now contains a larger contribution from Pd metal relative to PdO. Since this catalyst was exposed to a stoichiometric ratio of  $\text{CH}_4$  and  $\text{O}_2$  for the complete oxidation reaction of  $\text{CH}_4$  to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , this treatment is neither oxidative nor reductive and should not alter the relative amounts of PdO and Pd metal if they are in the ratios present under reaction conditions provided that activation barriers do not control the surface chemistry. However, annealing at  $180^\circ\text{C}$  promotes the reduction of PdO to Pd metal and the exposure to the  $\text{CH}_4$  and  $\text{O}_2$  mixture at  $180^\circ\text{C}$  further increases the amount of Pd metal relative to PdO in the near-surface region according to the XPS data. Also, the Pd signal is reduced relative to the Zr signal by these treatments. Since the total amount of Pd in the near-surface region remains unchanged, this signal reduction must be due to a matrix effect, i.e., a redistribution of the elements in the near-surface region (37). This matrix effect may involve agglomeration of the Pd.

A C  $1s$  spectrum obtained from the catalyst after heating at  $180^\circ\text{C}$  in vacuum is shown in Fig. 9a. Based on the peak size and the signal-to-noise ratio, a very small amount of C contamination remains after this treatment. This contamination is present both as hydrocarbon species and as an oxidized form of contamination (probably alcohols) with a higher BE value of approximately 285.3 eV. The C  $1s$  spectrum taken from the catalyst surface after exposure to the  $\text{CH}_4$  and  $\text{O}_2$  mixture at  $180^\circ\text{C}$  is shown in Fig. 9b. A large hydrocarbon feature is evident due to the adsorption of the  $\text{CH}_4$  from the reactant mixture. Furthermore, two other distinct features are evident. One is due to the presence of an adsorbed CO species, and another is due to a  $\text{CO}_3^-$  or  $\text{HCO}_3^-$  species (30). The dissociative adsorption of  $\text{CH}_4$  on

Pd metal (36) or the oxide support is the initial step in the reaction process. The presence of these  $\text{CH}_x$  species accounts for the increased size of the hydrocarbon peak. No features due to the presence of hydrogen-containing CO complexes are observable in the spectrum shown in Fig. 9b. This fact is consistent with removal of all of the hydrogen atoms from the carbon, resulting in the formation of a highly reactive adsorbed carbon species, which then reacts with neighboring oxygen to form an adsorbed CO species which next reacts with a surface oxygen and a hydroxyl group to form a bicarbonate species which decomposes to form a desorbing  $\text{CO}_2$  molecule (38–41). The surface hydroxyl group remains to catalyze more adsorbed CO to  $\text{CO}_2$ . The desorption of CO would be expected to occur in excess concentrations of methane relative to oxygen as observed under conditions where the oxygen is completely consumed (29). Since no adsorbed carbon states are observed in Fig. 9b, the step involving the oxygen addition to this species must be very rapid. Pd carbonyl ( $\text{Pd}_x(\text{CO})_y$ ) complexes have been observed on model Pd/ $\text{Al}_2\text{O}_3$  samples (42), but they decompose at very low temperatures (approximately 180 K) unless present on larger Pd islands. The catalyst examined in this study contains a mixture of PdO and Pd metal after the treatment in the reaction chamber, and no evidence of carbonyls is observed. Over the model alumina-supported Pd catalyst examined by Klier *et al.* (36), the adsorbed CO structures desorb at approximately 450 K ( $\sim 180^\circ\text{C}$ ) and may desorb at higher temperatures from a highly defective surface such as a powder. Also, Wang *et al.* (43) identified the presence of carbon clusters at step edges of Pd(670) surfaces after the dissociative adsorption of methane. Furthermore, no hydrogen-containing carbon compounds desorb during temperature-programmed oxidation experiments from this single crystal surface, indicating that all of the hydrogen is removed from the carbon after adsorption but before oxidation. These facts are consistent with the XPS data obtained in this study.

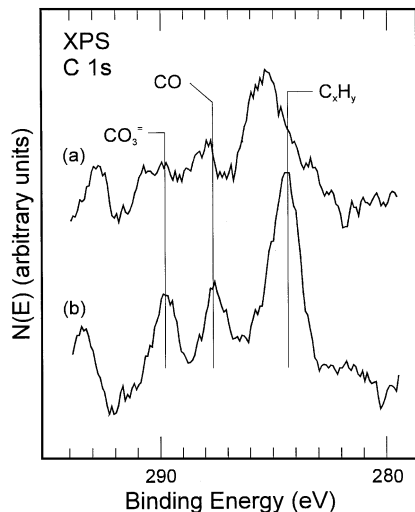


FIG. 9. High-resolution XPS C  $1s$  spectra obtained from the 5 wt% Pd/ZrO $_2$  catalyst after (a) heating at  $180^\circ\text{C}$  in vacuum for 45 min and (b) exposure to a 100 Torr mixture of 1 : 2  $\text{CH}_4$  and  $\text{O}_2$  at  $180^\circ\text{C}$  for 45 min.

## SUMMARY

The oxidation of methane using Pd/ZrO $_2$  catalysts has been examined under various test conditions. Calcining these catalysts at 110 or  $280^\circ\text{C}$  results in more active catalysts compared to catalysts calcined at 500 or  $800^\circ\text{C}$  for reactor operating temperatures above  $250^\circ\text{C}$ . A mild reductive treatment (flowing  $\text{H}_2$  over the catalyst at  $250^\circ\text{C}$ ) results in a catalyst with superior performance compared to a  $400^\circ\text{C}$  reductive pretreatment or no pretreatment. A mild oxidative treatment also improves the catalyst activity compared to a nontreated catalyst and is similar in performance to the catalyst reduced at  $250^\circ\text{C}$ . The effects of the Pd weight loading were examined as well. The rate increases as the amount of Pd increases up to 10 wt%, and little change in performance is observed at higher loadings. Decay studies

indicate that the activity of the Pd/ZrO<sub>2</sub> catalysts does not change over a 50-hr period under the reaction conditions used, although the activity of an optimized Pd/Al<sub>2</sub>O<sub>3</sub> catalyst initially increases and then decreases. These data indicate that Pd/ZrO<sub>2</sub> catalysts are superior to Pd/Al<sub>2</sub>O<sub>3</sub> catalysts with regard to both activity and decay for the catalytic oxidation of methane over the parameter ranges examined.

A surface characterization study of a 5 wt% Pd/ZrO<sub>2</sub> methane oxidation catalyst was performed using XPS before and during heating the catalyst at 180°C in vacuum and after exposure to 100 Torr of a 2:1 O<sub>2</sub> and CH<sub>4</sub> mixture at 180°C in an attached reaction chamber. The as-entered Pd/ZrO<sub>2</sub> catalyst consists of ZrO<sub>2</sub>, PdO, some Pd metal, PdO<sub>2</sub>, and a small amount of carbon-containing contamination. Heating the catalyst to 180°C (the approximate temperature at which the CH<sub>4</sub> oxidation reaction begins) reduces some of the PdO to Pd metal. Exposure to 100 Torr of a 2:1 mixture of O<sub>2</sub> and CH<sub>4</sub> at 180°C in an attached reaction chamber results in the formation of adsorbed CH<sub>x</sub>, CO, and carbonate or bicarbonate species. Based on these data a mechanism can be suggested in which the hydrogen bonds are first broken, leading to the formation of an adsorbed carbon species which bonds with surface O to form an adsorbed CO species. This CO species then forms a carbonate or bicarbonate species which decomposes to form CO<sub>2</sub>. This reaction is catalyzed by the bare support but not by reduced Pd metal supported on alumina. However, the addition of Pd improves the performance of the catalyst. This may be due to the fact that CH<sub>4</sub> dissociatively chemisorbs on Pd metal at a higher rate than zirconia and then spills over to the oxide support or Pd oxides, where it reacts.

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