

# Factors Affecting the Catalytic Activity of Pd/ZrO<sub>2</sub> for the Combustion of Methane

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The catalytic combustion of CH<sub>4</sub> has been investigated over Pd/ZrO<sub>2</sub> with the aim of identifying how the state of oxidation of the Pd affects the catalytic activity, particularly at low temperatures. It is found that fully reduced Pd is inactive and that the activity increases at 533 K until a plateau in activity is achieved when 6–7 ML of PdO have formed over the surface of the Pd crystallites. The maximum activity is identical to that for fully oxidized Pd. Examination of the PdO formed under reaction conditions and during oxidation in O<sub>2</sub> at 533 K reveals some differences. Temperature-programmed reduction in CH<sub>4</sub> and Raman spectroscopy demonstrate that the oxide formed under reaction conditions is largely crystalline PdO, whereas the oxide formed in O<sub>2</sub> is a mixture of amorphous and crystalline PdO. The crystalline form of PdO is found to reduce more readily than the amorphous form. It is observed that the low-temperature CH<sub>4</sub> combustion activity of PdO can be enhanced by producing a small amount of metallic Pd on the surface of PdO. The metallic Pd is more effective than PdO for the dissociative adsorption of CH<sub>4</sub>. It is hypothesized that the products of CH<sub>4</sub> adsorption on Pd, H<sub>s</sub> and CH<sub>x,s</sub> (x = 3–1), rapidly diffuse to the Pd/PdO interface and then reduce the PdO to Pd. The effects of metallic Pd cannot be sustained, though, under steady-state conditions, because the metallic Pd is oxidized back to PdO. © 1998 Academic Press

## INTRODUCTION

Palladium has been found to be more active than other transition metals for the combustion of methane (see, for example, Refs. (1, 2) and references cited therein), and consequently studies have been undertaken to identify the factors that influence the activity of Pd. Oh *et al.* (3) have suggested that adsorbed oxygen inhibits CH<sub>4</sub> oxidation because O atoms migrate into the bulk of Pd forming an unreactive PdO. The active form of the catalyst is proposed to be a thin layer of PdO on metallic Pd and bulk PdO is claimed to be inactive. Burch and Urbano (4) have shown that while metallic Pd is inactive, as is a monolayer of O on Pd, the activity of Pd/Al<sub>2</sub>O<sub>3</sub> increases until 3–4 ML of O as PdO have been accumulated on the surface of Pd particles under reaction conditions, whereafter the activity does not increase with further oxidation. However, bulk PdO is found to have

the same activity as a PdO film on Pd. The reconstruction of Pd particles during CH<sub>4</sub> combustion has been proposed by Garbowski *et al.* (5) to facilitate the increase in activity which occurs upon oxidation of Pd. These authors observe that the Pd crystallites on fresh Pd/Al<sub>2</sub>O<sub>3</sub> exhibit mainly Pd(111) planes, but after reaction these planes are transformed to Pd(200) surfaces. It is proposed that the latter planes allow the reversible transition from surface Pd to PdO without drastic change of lattice parameters.

Several ideas concerning the mechanism of CH<sub>4</sub> combustion over supported Pd catalysts have been reported. Müller *et al.* (6) have suggested that CH<sub>4</sub> combustion occurs via the Mars Van Krevelan mechanism in which O<sub>2</sub> is assumed to oxidize the surface of Pd thereby producing a surface oxide which is then reduced by CH<sub>4</sub>. A somewhat different mechanism has been proposed by Fujimoto *et al.* (7). These authors suggest that the critical step in the mechanism is the dissociative adsorption of methane at a pair of sites on the surface of PdO, one of which is an anionic vacancy and the other an O<sup>2-</sup> anion. The fragments produced in this process then rapidly reduce the surface of PdO forming additional anionic vacancies. O<sub>2</sub> is assumed to reoxidize the catalyst by dissociative adsorption on a pair of anionic vacancy sites. The rate expression developed on the basis of the proposed mechanism is found to be consistent with the observed kinetics. More recently Su *et al.* (8) have investigated the reduction of PdO by CH<sub>4</sub>. The reduction of PdO was found to occur via a nucleation mechanism requiring the initial formation of small particles of metallic Pd. The authors propose that dissociative adsorption of CH<sub>4</sub> on the Pd particles produces adsorbed H<sub>s</sub> and CH<sub>x,s</sub> (x = 1–3) species which then diffuse to the Pd/PdO interface where rapid reduction of the oxide occurs. These studies have raised the question of whether the presence of metallic Pd might not enhance the rate of CH<sub>4</sub> oxidation. With this in mind, the present investigation was carried out to determine the dependence of CH<sub>4</sub> combustion on the state of Pd oxidation, the reactivity of the PdO present, and the possibility of maintaining small amounts of Pd in combination with PdO at the surface of the catalyst.

## EXPERIMENTAL

All of the studies were performed with a 9.91 wt% Pd/ZrO<sub>2</sub> prepared by incipient wetness impregnation of zirconia with a solution of Pd(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> in nitric acid. The catalyst was air dried and then calcined in pure O<sub>2</sub> at 773 K. The final product is identical to that used in our studies of the oxidation and reduction of Pd/ZrO<sub>2</sub> (8). When fully reduced, the supported particles of Pd are estimated to have a particle diameter of 28 nm.

The experimental apparatus has been described in detail in Ref. (8). Measurements of catalyst activity and temperature-programmed reduction (TPR) were carried out in a quartz microreactor contained within an electrically heated furnace. He (99.999% Bay Airgas), H<sub>2</sub> (99.9999%, Air Products), CH<sub>4</sub> (99.97%, Matheson), and O<sub>2</sub> (99.999%, Air Products) were supplied to the reactor from a gas manifold. The reactor effluent was monitored by a quadrupole mass spectrometer interfaced to a personal computer for data acquisition. For a typical experiment, 0.272 g of catalyst was used. The feed gas contained 3% CH<sub>4</sub> and 5% O<sub>2</sub>, with the balance being He. The total flow rate of the feed gas was 60 cm<sup>3</sup>/min.

## RESULTS

To achieve a stable activity for methane oxidation and a reproducible TPR profile, it was found necessary to allow the catalyst to undergo a series of oxidation and reduction cycles. During break in both the TPR profile and the catalyst activity changed gradually, the changes becoming progressively smaller with increasing number of oxidation/reduction cycles. Figure 1 shows TPR profiles taken following oxidation of a freshly prepared sample of Pd/ZrO<sub>2</sub>, and after oxidation following 10 oxidation/reduction cycles.

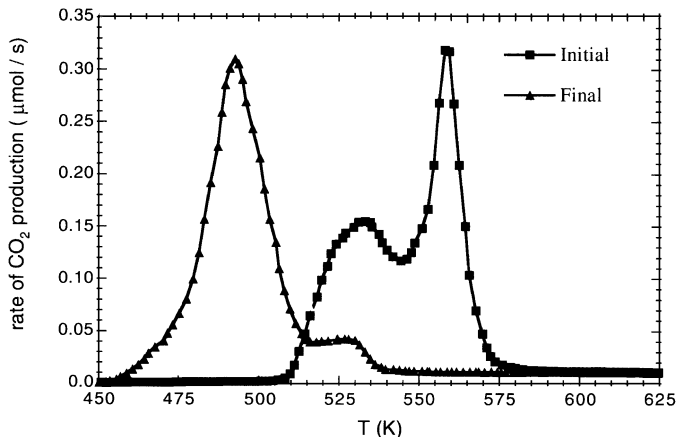


FIG. 1. TPR spectra for the reduction of Pd/ZrO<sub>2</sub> in CH<sub>4</sub> following initial oxidation of the catalyst in O<sub>2</sub> at 773 K and after oxidation following repeated oxidation and reduction.

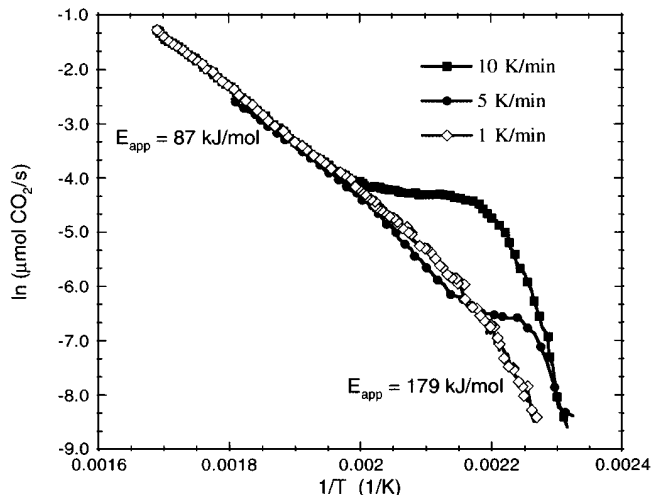


FIG. 2. Arrhenius plots for the combustion of CH<sub>4</sub> shown for different heating rates. Prior to each experiment the catalyst is fully oxidized in O<sub>2</sub> at 773 K.

In each case, oxidation was carried out for 30 min in pure O<sub>2</sub> at 773 K and reduction was carried out for 30 min in 3% CH<sub>4</sub> in He at 773 K. It is seen in Fig. 1 that the initial TPR spectrum shows two peaks for CO<sub>2</sub> located at 530 and 560 K. Both of these peaks are associated with the reduction of bulk PdO and the total integral under these peaks corresponds to an initial O/Pd ratio of 1.0, if the reduction is assumed to occur with the stoichiometry PdO + 0.25CH<sub>4</sub> → Pd + 0.25CO<sub>2</sub> + 0.5H<sub>2</sub>O. After repeated reduction and oxidation of the sample, the peak at 560 K disappears, the peak at 530 K is greatly reduced in intensity, and a new peak appears at 490 K, but the total area under the TPR profile remains the same. Further redox cycles have no effect on the TPR profile. The activity of the catalyst increased by nearly sixfold from the start to the end of the break-in period, when tested with a feed containing 3% CH<sub>4</sub> and 5% O<sub>2</sub> in He at 573 K. It is also notable that the dispersion of Pd in the reduced state did not change over the course of the break-in period.

Figure 2 shows the methane oxidation activity for a previously stabilized catalyst. If the catalyst is first oxidized for 1 h in O<sub>2</sub> at 773 K to assure complete oxidation of the Pd, then cooled to 298 K, and exposed to a mixture containing 3% CH<sub>4</sub> and 5% O<sub>2</sub> in He while the temperature is raised, the initial dependence of the rate of CO<sub>2</sub> formation on temperature depends on the heating rate. If the heating rate is 1 K/min, the data shown as open diamonds are obtained. Upon cooling the same set of data are obtained. Identical results are also obtained when the catalyst is allowed to achieve steady-state under isothermal reaction conditions. Two distinct branches of the Arrhenius plot are seen. Below 465 K the apparent activation energy is 179 kJ/mol and above 465 K the apparent activation energy is 87 kJ/mol. If

the initially preoxidized catalyst is heated at 10 K/min the data shown as closed squares are obtained. Below 455 K the rate of  $\text{CO}_2$  formation increases more rapidly with temperature than when the catalyst is heated at 1 K/min. The rate of reaction then becomes nearly independent of the temperature between 455 and 500 K, and finally above 500 K it increases with temperature at the same rate as that observed in the case where the catalyst is heated at 1 K/min. If the catalyst is allowed to cool at the end of this experiment, the activity profile is identical to that defined by the open diamonds, and when the catalyst is heated at 10 K/min a second time, the dependence of the rate of  $\text{CO}_2$  formation on the temperature is identical to that observed for a heating rate of 1 K/min. However, the data shown by the closed squares can be obtained again if the catalyst is first oxidized in  $\text{O}_2$  for 1 h at 773 K. Heating the catalysts at 5 K/min produces the data shown as closed circles. In this case, the initial dependence of the rate of  $\text{CO}_2$  formation on temperature is identical to that observed for a heating rate of 10 K/min, but the transition to a dependence identical to that observed for a heating rate of 1 K/min now occurs at 445 to 500 K. Finally, it was observed that if the catalyst was calcined in  $\text{O}_2$  for 1 h at 773 K, heated to 463 K at 10 K/min, and then held at this temperature, the rate of  $\text{CO}_2$  formation decreased over a 2–3-min period from the rate versus temperature curve described by the closed square to that described by the open diamonds.

As already noted, above 500 K the dependence of the rate of  $\text{CH}_4$  combustion on temperature is independent of the rate of catalyst heating. In this regime the kinetics of  $\text{CO}_2$  formation and  $\text{CH}_4$  consumption are known to be inversely dependent on the partial pressure of water (9). Since the rate data shown in Fig. 2 were acquired at constant space velocity, rather than constant  $\text{CH}_4$  conversion, the Arrhenius plot must be corrected for the variation in the degree of  $\text{H}_2\text{O}$  inhibition with increasing temperature. Correction for inhibition by  $\text{CO}_2$  can be neglected because the  $\text{CO}_2$  partial pressures occurring in the experiments shown in Fig. 2 are small (9). Assuming the stoichiometry of  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ , it is readily shown that the intrinsic activation barrier for  $\text{CH}_4$  combustion is twice the value of the apparent activation energy. As noted in

TABLE 1

Apparent Activation Energy for  $\text{CH}_4$  Combustion over Pd  
Corrected for Inhibition by  $\text{H}_2\text{O}$

Catalyst	$E_{\text{app}}$ , kJ/mol	Ref.
10% Pd/ZrO <sub>2</sub>	174	This work
10% Pd/ZrO <sub>2</sub>	170	(9)
0.9–5% Pd/ZrO <sub>2</sub>	184	(7)
11% Pd/Al <sub>2</sub> O <sub>3</sub>	168	(10)
3% Pd/Al <sub>2</sub> O <sub>3</sub>	178	(10)

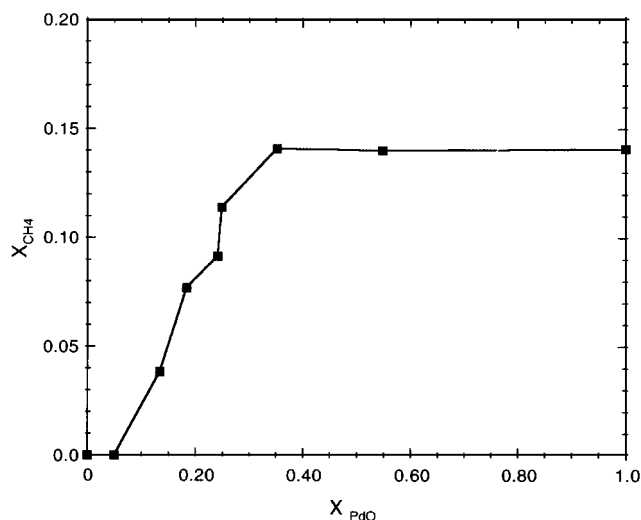


FIG. 3. Plots of methane conversion,  $x_{\text{CH}_4}$ , and extent of Pd oxidation,  $x_{\text{PdO}}$ , versus time under reaction conditions.

Table 1, the value of 174 kJ/mol obtained for the intrinsic activation energy in this study agrees well with values reported earlier for Pd/ZrO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> (7, 9, 10). It should be noted in this connection that no correction was made for  $\text{CO}_2$  inhibition, since this effect occurs only at  $\text{CO}_2$  partial pressures significantly greater than those encountered in this study (9).

A series of experiments was conducted to determine the dependence of the activity of the catalyst on the state of its oxidation. In the first set of experiments, the catalyst was first reduced to metallic Pd at 773 K in  $\text{H}_2$ . The temperature was then lowered to 533 K and the catalyst exposed to 3%  $\text{CH}_4$  and 5%  $\text{O}_2$  in He flowing at 60  $\text{cm}^3/\text{min}$ , while the activity was monitored as a function of time. After a prescribed time, the reaction was quenched by rapidly cooling the reactor to room temperature while passing He through it. Careful examination showed that the quench process had no effect on either the structure or the oxygen content of the catalyst. A TPR in  $\text{CH}_4$  was then carried out to determine the amount of oxygen associated with the Pd. Figure 3 illustrates how the conversion of methane,  $x_{\text{CH}_4}$ , and the extent of Pd oxidation,  $x_{\text{PdO}}$ , depend upon the duration that the catalyst has been under reaction conditions. It is evident that the activity of the catalyst is zero initially and that it rises with increasing time on-stream. The value of  $x_{\text{PdO}}$  attains the value of 0.05 almost instantaneously, corresponding to the accumulation of one monolayer of O atoms on the surface of the Pd particles; then it increases more slowly as the Pd undergoes bulk oxidation.

In a second set of experiments, a reduced catalyst was preoxidized in  $\text{O}_2$  for 1 h at 573, 673, and 773 K to obtain values of  $x_{\text{PdO}}$  corresponding to 0.35, 0.55, and 1.00. After each preoxidation, the catalyst was cooled to 533 K and then exposed to the  $\text{CH}_4/\text{O}_2$  mixture to determine the activity.

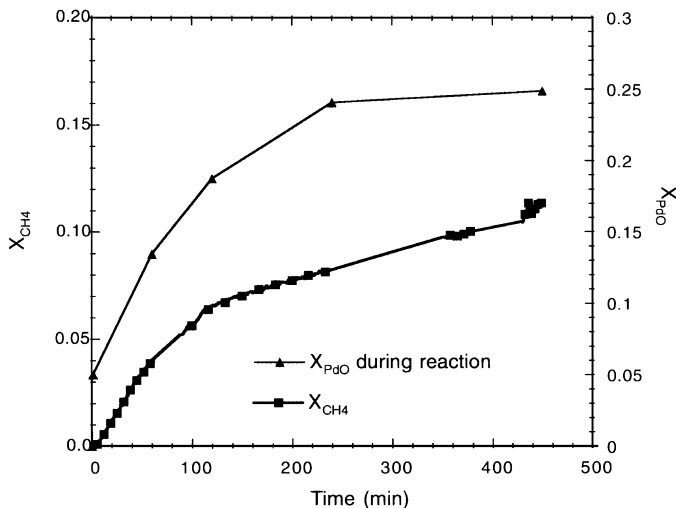


FIG. 4. A plot of the effect of extent of Pd oxidation,  $x_{\text{PdO}}$ , on the instantaneous conversion of CH<sub>4</sub>,  $x_{\text{CH}_4}$ .

As seen in Fig. 4, the activity is completely independent of  $x_{\text{PdO}}$  for  $x_{\text{PdO}} > 0.35$ . Also shown in this plot are the data presented in Fig. 3. In this case, it is seen that the activity rises above zero only when the value of  $x_{\text{PdO}}$  exceeds 0.05 and then increases almost linearly. Taken together, the data in Fig. 4 show that the conversion of methane does not increase further once  $x_{\text{PdO}} = 0.3$ – $0.35$ , which corresponds to about 6–7 ML of PdO.

Several experiments were undertaken to ascertain whether the oxidation of Pd under reaction conditions produces an oxide that is different from that obtained by oxidation in O<sub>2</sub>. Figure 5 compares the dependence of  $x_{\text{PdO}}$  on time when Pd is oxidized in 5% O<sub>2</sub> in He and in a mixture of 3% CH<sub>4</sub> and 5% O<sub>2</sub> in He. In both cases the oxidation temperature is 533 K. Oxidation in O<sub>2</sub> alone proceeds somewhat more rapidly initially but then it slows down relative to the rate of oxidation in a reaction mixture. However, after 450 min, the extent of oxidation in both cases is comparable. The gas composition does have an effect, though, on the TPR profile of the deposited oxide, as can be seen by reference to Fig. 6. When oxidation occurs in pure O<sub>2</sub> (see panel (a)), at least three TPR peaks are observed. After 1 h of oxidation, these features are centered at 600, 520, and 480 K. The peak at 600 K has been observed in our earlier studies of the oxidation of Pd/ZrO<sub>2</sub> and is attributable to the reduction of a monolayer of atomic oxygen on the surface of metallic Pd (8). The other two peaks are attributable to different forms of PdO. As the duration and extent of oxidation increases these peaks shift in both location and relative intensity in a complex fashion, but as the value of  $x_{\text{PdO}}$  approaches 0.25, the peak at 470 K becomes the most intense feature in the spectrum. If the oxidation were continued longer or were carried out at higher temperature, then the TPR spectrum would have been dominated

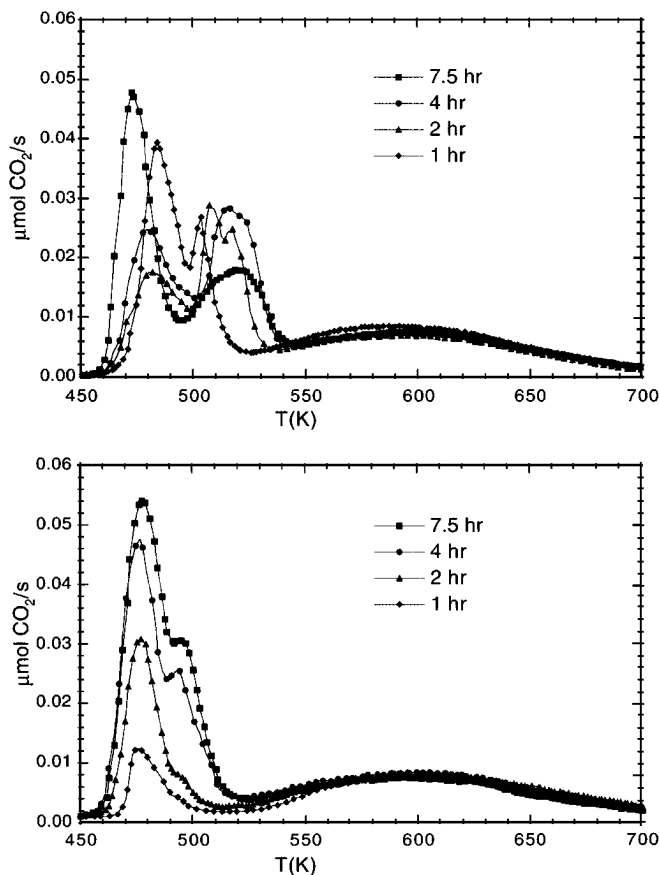


FIG. 5. A comparison of the extent of oxidation of Pd,  $x_{\text{PdO}}$ , with time during oxidation in O<sub>2</sub> (5%) and in a mixture of CH<sub>4</sub> (3%) and O<sub>2</sub> (5%) at 533 K.

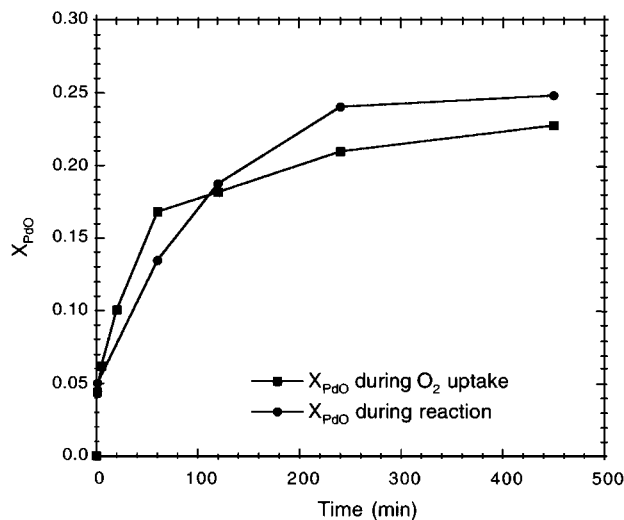


FIG. 6. TPR spectra for the reduction of Pd/ZrO<sub>2</sub> in CH<sub>4</sub> (3%) following (a) oxidation in O<sub>2</sub> (5%) and (b) in CH<sub>4</sub> (3%) and O<sub>2</sub> (5%) at 533 K. The extent of Pd oxidation,  $x_{\text{PdO}}$ , after a given period of oxidation is shown in Fig. 5.

by the feature at 470 K associated with the reduction of fully crystalline PdO (8). Since the initial oxidation of Pd is known (8) to produce an amorphous oxide which then transforms into crystalline PdO, it is reasonable to suggest that the peak(s) appearing in the vicinity of 510–530 K are associated with the reduction of amorphous PdO. When oxidation of Pd occurs under reaction conditions, two TPR peaks are observed at 475 and 500 K, together with the peak at 600 K. As oxidation proceeds, the positions of the two low-temperature peaks do not change, and the peak at 475 K rapidly becomes the dominant feature in the spectrum. Raman spectra of the oxide formed during oxidation in O<sub>2</sub> and during CH<sub>4</sub> oxidation also provided evidence for differences in the structure of PdO. In both cases a band is observed at 651 cm<sup>-1</sup>, characteristic of crystalline PdO (10). However, for an equivalent amount of oxide, the intensity of this band is greater when the oxide is deposited under reaction conditions. Based on the results of our study of the oxidation of Pd to PdO, this observation suggests that the fraction of the deposited oxide occurring as crystalline PdO is greater when the oxide is formed under reaction conditions. At higher temperatures, the differences in oxide structure would be expected to disappear, since it has been shown, that the transformation of amorphous to crystalline PdO proceeds rapidly at temperatures above 573 K (8).

In a related study (8) it was noted that the presence of metallic Pd in contact with PdO facilitates the reduction of PdO by CH<sub>4</sub>, since the activation of CH<sub>4</sub> occurs more readily on Pd than PdO. It was reasoned, therefore, that if small amounts of metallic Pd could be deposited on the surface of PdO, this might enhance the rate of CH<sub>4</sub> combustion. To test this hypothesis, experiments were conducted in which small pulses of H<sub>2</sub> were injected into a stream containing a mixture of CH<sub>4</sub> and O<sub>2</sub> passed over a fully oxidized sample of Pd/ZrO<sub>2</sub> maintained at temperatures very near the light-off temperature for CH<sub>4</sub> combustion. The amount of H<sub>2</sub> in each pulse was 5.75 μmol and the interval between pulses was 20 s. H<sub>2</sub> was used as the reducing agent, since previous studies (8) had shown that this reducing agent would produce metallic Pd in intimate contact with PdO. Figure 7 shows that at 398 K, the first three pulses of H<sub>2</sub> are consumed completely, without having any effect on the rate of CO<sub>2</sub> formation. Subsequent pulses of H<sub>2</sub> produce a noticeable rise in the rate of CO<sub>2</sub> formation, but after passage of the seventh pulse, the rate relaxes back to zero. A similar pattern was observed at 423 K, but in this case the effect of H<sub>2</sub> became evident after two pulses. When the temperature was raised to 453 K, which is just above the threshold for the onset of CH<sub>4</sub> combustion, the effects of pulsing H<sub>2</sub> became evident, even after just one pulse. The maximum in the rate of CO<sub>2</sub> formation occurs after the introduction of three pulses, whereafter further pulses of H<sub>2</sub> produce a momentary rise in the rate of CO<sub>2</sub> formation, but the over-

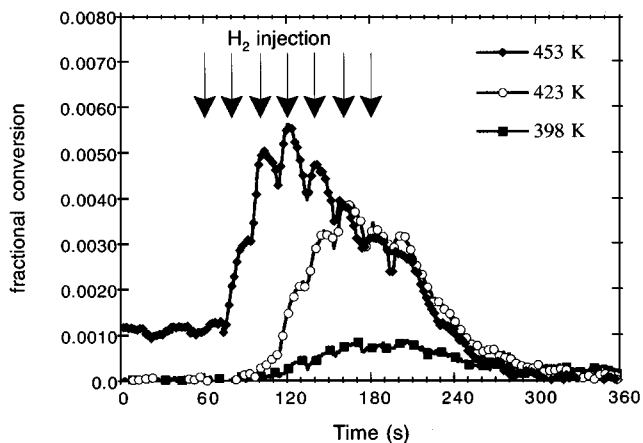


FIG. 7. The effect of injecting pulses of H<sub>2</sub> (5.75 μmol) into a mixture of CH<sub>4</sub> (3%) and O<sub>2</sub> (5%) on the conversion of CH<sub>4</sub>, x<sub>CH<sub>4</sub></sub>.

all rate declines monotonically to zero. No rise in catalyst temperature was observed when the H<sub>2</sub> pulses were introduced at 398 and 423 K, and the catalyst temperature rose less than 4 K when the H<sub>2</sub> pulses were introduced at 453 K.

To see whether metallic Pd could be maintained on the surface of PdO during CH<sub>4</sub> combustion, a small amount of H<sub>2</sub> (0.01 to 0.1%) was added to the CH<sub>4</sub>/O<sub>2</sub> feed. While the added H<sub>2</sub> was quantitatively oxidized to H<sub>2</sub>O at 398 K, no enhancement in the rate of CH<sub>4</sub> oxidation was observed. At 498 K, a reduction in the rate of CH<sub>4</sub> combustion was observed relative to that measured in the absence of H<sub>2</sub> addition. This latter effect is attributed to the known inhibition of CH<sub>4</sub> combustion by water vapor.

In a second set of experiments, a fully oxidized sample of Pd/ZrO<sub>2</sub> was partially reduced in either H<sub>2</sub> or CH<sub>4</sub> and then placed under reaction conditions to see whether the presence of metallic Pd might enhance the initial activity of the catalyst. Figure 8 shows a plot of the instantaneous

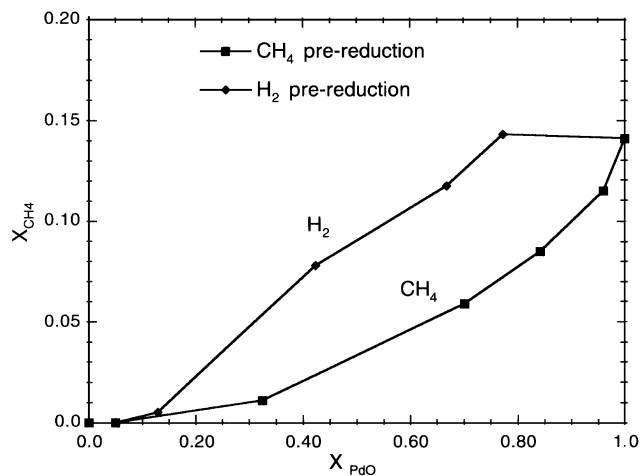


FIG. 8. The effect of prereducing Pd/ZrO<sub>2</sub> in H<sub>2</sub> and CH<sub>4</sub> on the instantaneous conversion of CH<sub>4</sub>, x<sub>CH<sub>4</sub></sub>.

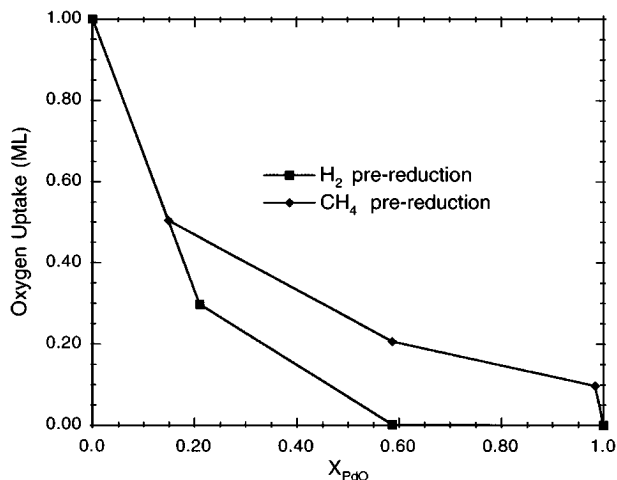


FIG. 9. The effect of prereducing fully oxidized Pd/ZrO<sub>2</sub> in H<sub>2</sub> and CH<sub>4</sub> on the uptake of O<sub>2</sub> at 298 K.

rate of CH<sub>4</sub> consumption as a function of the amount of PdO remaining in the catalyst,  $x_{\text{PdO}}$ . It is evident that pre-reduction of the catalyst in H<sub>2</sub> has no effect on the activity until more than 20% of the PdO has been reduced, whereafter the activity declines with further reduction, whereas pre-reduction in CH<sub>4</sub> has a negative effect, independent of the amount of the PdO reduced. To assess the amount of metallic Pd present after pre-reduction, O<sub>2</sub> was adsorbed at 298 K, after the catalyst had been cooled in He from 533 to 298 K. Figure 9 shows that when pre-reduction was carried out with H<sub>2</sub>, then no O<sub>2</sub> was adsorbed until more than 40% of the initial inventory of PdO had been reduced. By contrast, the O<sub>2</sub> adsorption is observed in all cases when pre-reduction is carried out in CH<sub>4</sub>, no matter how little of the initial inventory of PdO has been removed.

## DISCUSSION

The results presented in Figs. 3 and 4 show that at 533 K, chemisorbed oxygen present on the surface of metallic Pd is inactive for the oxidation of methane. This finding is consistent with the TPR profiles presented in Fig. 6 which show that this form of oxygen begins to react above 530 K and reaches maximum activity at 600 K. As seen in Fig. 4, the methane combustion activity of Pd/ZrO<sub>2</sub> increases linearly with increasing degrees of Pd oxidation and reaches a plateau at about  $x_{\text{PdO}} = 0.35$ , corresponding to about 7 ML of PdO. Increasing the extent of Pd oxidation above  $x_{\text{PdO}} = 0.35$  has no further effect on the catalyst, which means that only a relatively thin shell of PdO over a core of Pd is required to achieve high activity. All of these findings are in good agreement with those reported by Burch and Urbano (4) for CH<sub>4</sub> combustion at 573 K over Pd/Al<sub>2</sub>O<sub>3</sub>.

The results of both TPR and Raman investigations suggest that the palladium oxide deposited during the combus-

tion of CH<sub>4</sub> is crystalline PdO. Both the position and shape of the TPR spectrum seen in Fig. 6 closely resemble that observed for fully oxidized PdO/ZrO<sub>2</sub>, in which case the presence of crystalline PdO is confirmed by both XRD and Raman spectroscopy (7, 8, 11). The Raman spectrum of the oxide formed after 7.5 h of reaction at 533 K ( $x_{\text{PdO}} = 0.25$ ) also exhibits a well-defined peak at 651 cm<sup>-1</sup>, characteristic of crystalline PdO. The formation of crystalline PdO seems to be favored during Pd oxidation during CH<sub>4</sub> combustion, as opposed to oxidation in O<sub>2</sub> at the same temperature. The TPR spectra shown in Fig. 6 demonstrate that during oxidation in O<sub>2</sub> a significant portion of the deposited oxide appears to be amorphous PdO, and the transformation of this phase to crystalline PdO occurs relatively slowly. Raman spectra of the oxide deposited by O<sub>2</sub> oxidation show a band at 651 cm<sup>-1</sup>, but its intensity is less than that for an equivalent amount of oxide deposited during CH<sub>4</sub> combustion. As noted earlier, this observation is consistent with the proposal that only a portion of the oxide deposited during O<sub>2</sub> oxidation at 533 K is crystalline PdO (8).

The structure of the PdO affects its activity. This is clearly evident from the TPR spectra presented in Fig. 6, which show that the most active form of oxygen is that present in crystalline PdO, corresponding to the peak at 470 K. Amorphous PdO reacts at temperatures above 500 K. Further evidence for the relationship between the oxide structure and catalyst activity was obtained during the break-in of the catalyst used in these studies. The TPR spectra presented in Fig. 1 demonstrate that the reactivity of the oxide changes with repeated oxidation and reduction of the catalyst, ultimately achieving a state in which crystalline PdO can be formed reproducibly. Consistent with these changes, the catalyst activity increases as the oxide becomes more crystalline. The changes occurring during the break-in period may be associated with reconstruction of the Pd particle surface as has been suggested by Garbowski *et al.* (5).

The increase in the rate of CH<sub>4</sub> combustion following the injection of several pulses of H<sub>2</sub> into the CH<sub>4</sub>/O<sub>2</sub> feed is ascribed to the formation of small amounts of Pd on the surface of PdO. This interpretation is suggested by our studies of the reduction of PdO by CH<sub>4</sub> (8), where it was observed that the presence of metallic Pd in close contact with PdO greatly enhanced rate of reduction of PdO. Since CH<sub>4</sub> is not readily activated on PdO at low temperatures, but will dissociatively adsorb on metallic Pd (see Ref. (12) and references cited therein), it is proposed that the presence of metallic Pd produces H<sub>2</sub> and CH<sub>x,s</sub> ( $x = 1-3$ ) which then diffuse to the Pd/PdO interface where they can reduce the oxide. This mechanism of metal-assisted oxide reduction has recently been proposed as well, to explain the enhanced CO oxidation activity of Pt supported on reducible oxides such as Fe<sub>2</sub>O<sub>3</sub> and Co<sub>2</sub>O<sub>3</sub> (13). The influence of the metallic Pd is not sustained once the pulses of H<sub>2</sub> are terminated, because reoxidation rapidly converts the metal back to the oxide.

The accumulation of H<sub>2</sub>O on the catalyst surface produced by the oxidation of H<sub>2</sub> also serves to inhibit the oxidation of CH<sub>4</sub>. This latter effect would explain, as well, the reason why the addition of small amounts of H<sub>2</sub> to the CH<sub>4</sub>/O<sub>2</sub> feed fails to induce light-off of the catalyst at T < 450 K, and at higher temperatures it actually decreases catalyst activity.

The attempts to produce metallic Pd by prereduction in either H<sub>2</sub> or CH<sub>4</sub> were also unsuccessful in enhancing the activity of the catalyst. As seen in Fig. 8, prereduction in H<sub>2</sub> has no effect on the initial activity of the catalyst for  $x_{\text{Pd}} < 0.2$ , and above this level leads to a monotonic decrease in the activity. This behaviour can be explained in the following way. When the level of reduction is small, the Pd film formed over the oxide is rapidly reoxidized by diffusion of oxygen through the film. When  $x_{\text{Pd}} > 0.2$  the amount of Pd covering the oxide now exceeds 1 ML, and consequently, access to the oxide is inhibited. Partial reduction of PdO in CH<sub>4</sub> has a negative effect on the initial activity of the catalyst, no matter how little PdO is removed. The reason for this is that CH<sub>4</sub> reduction leads to the formation of Pd particles on the surface of the remaining PdO, rather than a film of Pd, as is the case when H<sub>2</sub> is used as the reducing agent (8). The Pd particles rapidly acquire a monolayer of oxygen which, as discussed above, is much less active for CH<sub>4</sub> oxidation than PdO.

The transient formation of metallic Pd is believed to be responsible for the anomalously high rate of CH<sub>4</sub> oxidation observed when the catalyst is heated at a rate of either 5 or 10 K/min (see Fig. 2). It is proposed that rapid heating induces the nucleated reduction of PdO (8). The particles of Pd thus formed further accelerate the oxidation of CH<sub>4</sub>, but are eventually consumed via oxidation at higher temperatures, which then lowers the rate of CH<sub>4</sub> combustion. When the rate of catalyst heating is below 5 K/min, the dynamics of oxidation and reduction stay in balance, resulting in the presence of a negligible amount of metallic Pd. Consistent with this interpretation, we observe that the apparent activation energy for CH<sub>4</sub> oxidation during the initial portion of the temperature ramp (537 kJ/mol) is comparable to that measured for the initial reduction of the fully oxidized catalyst in CH<sub>4</sub> (502 kJ/mol) (8).

## CONCLUSIONS

The activity of freshly reduced Pd/ZrO<sub>2</sub> for methane combustion increases with time paralleling the increase in the oxidation of the supported Pd particles. At 533 K, a maximum activity is achieved when 6–7 ML of PdO are formed

over the Pd particles, and further oxidation of Pd has no effect on the catalytic activity. TPR profiles and Raman spectroscopy indicate that PdO deposited under reaction conditions at 533 K occurs as crystalline PdO, but that oxidation in O<sub>2</sub> at 533 K produces a mixture of amorphous and crystalline PdO. The activity of PdO for CH<sub>4</sub> combustion can be enhanced by partially reducing the surface of the oxide to produce a small amount of metallic Pd. Metallic Pd is produced by either injecting small pulses of H<sub>2</sub> into a flowing mixture of CH<sub>4</sub> and O<sub>2</sub>, or by very rapid heating of fully oxidized Pd/ZrO<sub>2</sub> in the reaction mixture. The metallic Pd serves to dissociate CH<sub>4</sub> more effectively than PdO, and the products formed there by, e.g., H<sub>s</sub> and CH<sub>x,s</sub> (x = 3–1), diffuse to the Pd/PdO interface where they rapidly reduce the PdO. However, the effects of metallic Pd cannot be sustained under steady-state conditions because with time the particles of Pd are reoxidized back to PdO. Nevertheless, the results of this study suggest that the methane combustion activity of PdO might be enhanced by deposition of small particles of a metal that can dissociate CH<sub>4</sub>, but does not undergo oxidation for the conditions used. Such an additive could enhance the low-temperature activity of Pd for methane combustion.

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