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Surface Area Increase on Pd Foils after Oxidation in Excess Methane

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An increase in the PdO surface area by a factor of about 20 was observed after treatment of Pd foils in excess methane at 598 K. The surface area was increased as the O_2 partial pressure in the activation treatment was decreased. The activated foil was probed by the reaction of complete oxidation of methane in excess O_2. The rate was proportional to the PdO surface area and thus the turnover rate per unit of PdO area was the same as that for the untreated foil. Critical for this assessment was the determination of the PdO surface area measured by exchange of surface oxygen with $^{18}O_2$. The PdO surface area decreased after interaction with water when the sample was cooled. After treatment of the foil in excess methane, PdO but not Pd was identified by X-ray photoelectron spectroscopy, and carbon deposits from methane were identified on the surface and in the bulk by temperature-programmed desorption. © 2001 Academic Press

Key Words: **Pd foil; PdO morphology; methane combustion; ^{18}O isotope exchange; PdO surface area measurement.**

1. INTRODUCTION

The combustion of methane in excess O_2 over Pd catalysts is important for the generation of energy in gas turbines and for the abatement of methane emissions in the exhaust of gas-powered engines. One problem for the former application is that even though Pd is the most active metal for the combustion of methane, the rate on Pd is not sufficiently high to light off the catalyst at the flow rate and temperature at which the lean methane mixture contacts the catalyst in a turbine (about 300°C) (1, 2). Thus, a more active catalyst would be highly desirable. There have been reports in the literature (3–5) that in the oxidation reaction (with O_2) in excess hydrocarbon on a Pd foil, the overall rate of oxidation of the hydrocarbon is increased as compared to the rate of the reaction in excess O_2. The objective of this contribution was to investigate how a treatment in excess methane on a Pd foil could increase the rate of oxidation in excess O_2. The techniques of scanning electron microscopy, temperature-programmed desorption, and kinetic measurements confirmed that the PdO surface area increased dramatically after a treatment in excess methane but that the turnover rate per unit of PdO surface area remained the same for the oxidation of methane under excess O_2. The oxidation treatment in excess hydrocarbon may be useful for activating samples with Pd particles of large enough size to resemble a foil. However, the surface area of PdO decreased after activation due to an interaction with water generated during the test reaction (methane oxidation in excess O_2). The practical application of this activation treatment is limited by the PdO loss of surface area but the treatment may still be useful in some applications.

2. EXPERIMENTAL METHODS

The combustion of methane on Pd foils was performed at atmospheric pressure in a batch reactor attached to an ultrahigh-vacuum (UHV) surface analysis chamber described elsewhere (6). The palladium catalysts were 0.1-mm-thick polycrystalline foils (Alfa Aesar, 99.9%) with a geometric surface area of $\sim$1.0 cm^2. The foil was spot-welded between two stainless steel pins attached to a Macor sample holder. The temperature was measured by using a chromel–alumel thermocouple spot-welded directly on the palladium foil. The sample was heated resistively. The sample holder could be rotated inside the UHV chamber for analyses by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption (TPD). Samples were cleaned before reaction as described before (6).

Reactions were carried out in a 840-cm^3 batch reactor with gases being introduced from a gas manifold in the following order: N_2 (624 Torr), O_2 (160 Torr for excess O_2 or 16 Torr for excess methane), and finally CH_4 (16 Torr for excess O_2 and 160 Torr for excess methane). The reactants were mixed by a Metal Bellows pump model MB-21 at a nominal rate of 1000 cm^3 min^{-1} for 25 min before the foil was heated to reaction temperature (598 K). To avoid carbon deposition on the catalyst surface for the reaction in excess methane, the reaction was carried out up to the point where a maximum of 80% of the O_2 was consumed. The gas-phase composition was analyzed by using a HP

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6890 Series gas chromatograph (GC) equipped with a 15-ft Carboxen 1000, 60/80 mesh column and a thermal conductivity detector (TCD). The sampling (every 18 min) was performed with an automatic sampling valve. After reaction, the sample was moved back into the UHV chamber (without exposure to the atmosphere) for surface analysis by AES, XPS, and TPD.

Because the surface area of the catalyst is small ($\sim$1 cm^2), two experiments were performed to measure the background activity of the catalytic reactor. In the first experiment a stainless steel foil was used in place of the Pd foil under standard reaction conditions. Based on the detection limit of our GC, the background rate is lower than 1×10^{-5} s^{-1} compared to the steady-state activity of 59×10^{-2} s^{-1} for a Pd foil under standard conditions (16 Torr CH_4, 160 Torr O_2, 1 Torr H_2O, N_2 balance to 800 Torr, and 598 K). In the second experiment, a Pd foil was used in the reaction under standard conditions without cleaning. The initial reaction rate was 6×10^{-2} s^{-1} under standard conditions, but decreased to zero after about 30 min of reaction, due to the migration of impurities to the surface. This experiment simulates the contribution of the back of the foil, which cannot be cleaned by sputtering, and at steady-state the rate is expected to be negligible.

XPS spectra were collected using Mg $K\alpha$ (1253.6 eV) or Al $K\alpha$ (1486.6 eV) radiation at a power of 300 W. The XPS survey spectra were recorded by using an analyzer pass energy of 100 eV, whereas for the core level measurements of Pd 3*d*, O 1*s*, and C 1*s* the analyzer pass energy was 25 eV. The resolution measured at full width at half-maximum of the Pd $3d_{5/2}$ transition was 1.2 eV.

The TPD analysis was made by heating the sample under UHV conditions up to 873 K at a heating rate of 5 K s^{-1}. Desorption products were monitored by using an UTI-100C quadrupole mass spectrometer (MS). The $^{13}CH_4$ isotope of methane was used to discriminate between carbon dioxide signal originating from the oxidation of an impurity present in the reactor chamber and that from carbon incorporated on the surface or into the bulk structure of the foil deposited under reaction. Scanning electron microscopy (SEM) images were obtained at the Center for Materials Research and Engineering(CMSE) at the Massachusetts Institute of Technology with a FEI/Philips XL30 FEG ESEM model operating at 25.0 kV and secondary electron imaging (resolution at 30.0 kV is 3.5 nm).

3. RESULTS

The main results of this contribution are that the PdO surface area increased after treatment of a Pd foil in excess methane and that the rate of methane combustion under excess O_2 is strictly proportional to the PdO surface area. Thus, the turnover rate per unit of PdO area remained the same. Results on the reactivity of the foil, measurement of PdO surface area, and surface characterization by SEM, XPS, and TPD will be presented in turn. It is important to clarify that the activation treatment is carried out in excess methane and that the surface is probed by methane oxidation reaction carried out in excess O_2.

3.1. *Activation and Deactivation Behavior after Treatment in Excess Methane*

Foil activity will be reported as a nominal turnover rate (TOR). The appellation "nominal" is used to indicate that the number of active sites is taken to be invariant and equal to the initial number of Pd atoms on the surface of the clean foil, so changes in surface area are not taken into consideration. We have reported previously that the nominal TOR for a Pd foil in the combustion of methane under excess O_2 was 59×10^{-2} s^{-1} under the defined standard conditions of 160 Torr O_2, 16 Torr CH_4, and 1 Torr H_2O, at 598 K (6). The nominal TOR was 3 times higher than the highest TOR reported on supported catalysts. This is a benchmark rate to compare the activity of the foil after various treatments.

The reactivity of a Pd foil for the reaction of combustion of methane under excess O_2 was increased by an activation treatment of the foil under excess methane. The foil activation conditions were 16 Torr O_2, 160 Torr CH_4, N_2 balance to 800 Torr, at 598 K for 60 min, but note that the treatment was performed in a batch reactor and that the final O_2 pressure decreased to 4 Torr. Figure 1 shows that after foil activation, the nominal TOR is 19 times higher than the rate on a fresh foil for the reaction of methane oxidation in excess O_2. On subsequent reaction batches the nominal TOR dropped continuously as shown in Fig. 1 (continuous line). The procedure between reaction batches consisted of cooling the foil, evacuating the reactor, and charging a

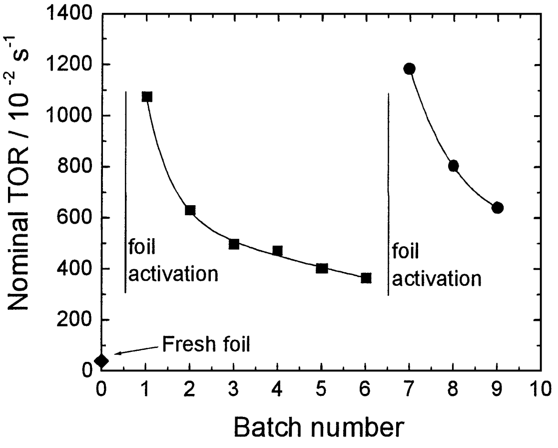

FIG. 1. Methane oxidation on Pd foil after foil activation in excess methane. Activation conditions were 598 K, 16–4 Torr O_2, 160 Torr CH_4, N_2 balance to 800 Torr. Batch reaction rates are reported at 550 K, 160 Torr O_2, 16 Torr CH_4, and 1 Torr H_2O, but reactions were carried out at 598 K, 160 Torr O_2, 16 Torr CH_4, N_2 balance to 800 Torr for 170 min.

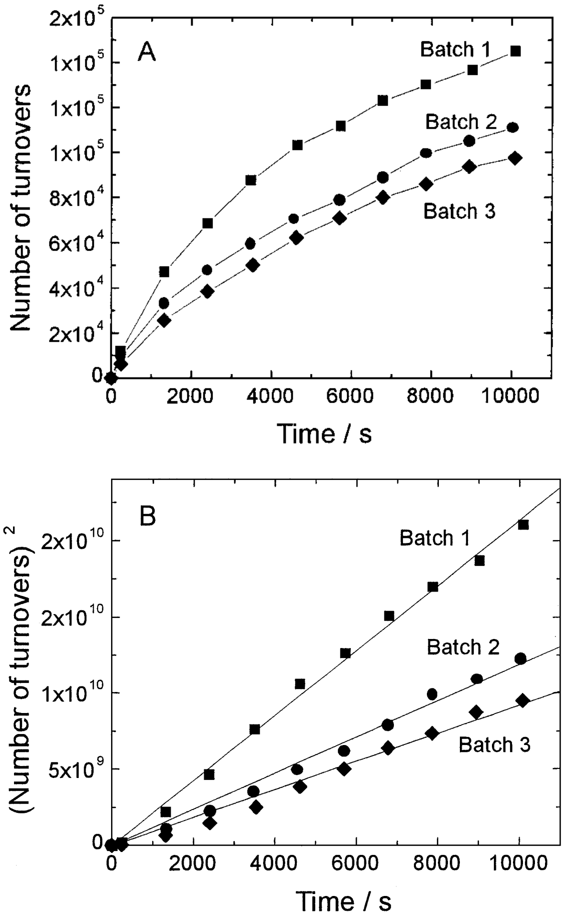

FIG. 2. (A) Number of turnovers (CH_4 molecules converted per surface Pd atom) as a function of time for batches 1 to 3 in Fig. 1 and (B) integrated equation plotted in linear form (H_2O inhibition accounted for).

new mixture. Note however that the sample can be reactivated by another treatment in excess methane (Fig. 1) and that an activated foil will return to the initial activity of a fresh foil after the standard cleaning procedure (annealing and sputtering) is carried out. In other words, the activation treatment is reversible.

The performance of the Pd foil as shown in Fig. 1 identifies two questions: what caused the sample to deactivate and what caused the sample to be more active? To answer the deactivation question, the effect of addition of H_2O and O_2 on the rates was explored. Figure 2A shows the accumulation plot for batches 1–3 in Fig. 1. All plots show a curvature due to water inhibition. The water inhibition effect shows a reaction order of approximately -1 for H_2O concentration (7) and can be accounted for by integration of the batch reactor equation (6, 8) with the results shown in Fig. 2B. Note that the slope of each line in Fig. 2B is proportional to the rate constant. Thus, the fact that the points in Fig. 2B are on a line shows that there is no deactivation during the reaction; there is only inhibition by water. The reversible water inhibition during the reaction (9, 10) implies that the rate should be restored when the reaction is repeated, as observed over successive runs on a foil not submitted to activation. Thus, the deactivation happens between the end of one reaction and the beginning of the next one. After six consecutive batch reactions, the initial reaction rate can be restored by a new pretreatment under excess methane (Fig. 1), with the same deactivation pattern appearing again.

To determine whether the cooling followed by reactor recharging triggers the loss of activity, a batch reaction was carried out on an activated foil for 170 min under excess O_2 at 598 K. Following the reaction, the reactor was cooled to room temperature, but the reactants and products were kept circulating inside the reactor for about 60 min. The temperature was then increased again to 598 K and the reaction continued for an additional 60 min. Comparison of the slopes of the integrated form of the rate equation, before and after the reaction was stopped, showed that the activity dropped by a factor of 2, reaching values similar to those obtained in Fig. 1 for batches 1 and 2. Thus, to trigger the sintering process the foil surface should be cooled, which is counterintuitive. Another possibility for the loss of activity is sample contamination during reactor evacuation and charging. However, a sample that did not go through an activation step with the same cooling procedure showed the same rate on consecutive batches; contamination is not a problem.

The quantification of the influence of O_2 and H_2O in causing foil deactivation was investigated next by activating the foil first and then measuring separately the effect of each modifier (Table 1). A treatment in O_2 at 598 K after foil activation had no effect in deactivating the foil. However, treatment with 5 or 10 Torr of water along with O_2 decreased the rate to about the same value as that after the first methane oxidation reaction in excess O_2 (cf. Fig. 1 and Table 1). Thus, deactivation is triggered by the presence of H_2O but not O_2.

TABLE 1

Influence of Different Treatments on the Nominal Turnover Rate for Methane Combustion in Excess O_2 of an Activated Pd Foil

Treatment after foil activation	Nominal TOR for test reaction[a] (10^{-2} s^{-1})
No treatment	1232
160 Torr O_2[b]	1259
160 Torr $O_2 + 5$ Torr of H_2O[b]	820
160 Torr $O_2 + 10$ Torr of H_2O[b]	644

[a] Turnover rates corrected for 550 K, 160 Torr O_2, 16 Torr CH_4, 1 Torr H_2O, N_2 balance to 800 Torr. Number of Pd sites was assumed constant and calculated from the initial geometric surface area of the clean foil.

[b] N_2 balance to 800 Torr was added. Treatment was carried out at 598 K for 170 min.

TABLE 2

Nominal TOR for the Oxidation of Methane after Foil Activation at Different O_2 Partial Pressures for 60 Min at 598 K

Partial pressure of O_2 on activation (Torr)[a]		
Initial	Final	Nominal TOR for test reaction (10^{-2} s^{-1})[b]
16	4	1232
24	12	1189
32	22	587
48	39	265

[a] In addition to O_2, 160 Torr CH_4 and N_2 balance to 800 Torr were added.

[b] Turnover rates corrected for 550 K, 160 Torr O_2, 16 Torr CH_4, 1 Torr H_2O, N_2 balance to 800 Torr. Number of Pd sites was assumed constant and calculated from the initial geometric surface area of the clean foil.

Next, the effect of the partial pressure of O_2 in the activation of the foil was tested. This is certainly an important variable since a treatment in excess O_2 produces a sample with a nominal turnover rate 19 times lower than that of a sample treatment in excess methane. The effectiveness of the sample activation treatment, as a measure of the rate of oxidation of methane in excess O_2, decreased as the amount of O_2 in the rich mixture increased from 16 to 48 Torr with a constant pressure of methane at 160 Torr, Table 2. It is important to note that the activation treatment is carried out in a batch reactor and because O_2 is the limiting reagent, its concentration varies substantially during the treatment. Since the effectiveness of the treatment is a function of O_2 pressure, one should be careful to choose appropriate experimental conditions to reproduce the results presented here and for this reason Table 2 lists the initial and final pressures of O_2.

3.2. *PdO Morphology and Surface Area Contributions to Rate Enhancement*

As stated previously, the results in Fig. 1 show an activation due to the treatment in excess methane. Scanning electron microscopy was used to image the surface after various treatments. Figure 3a shows the reference clean Pd foil. It shows a flat surface (at the chosen magnification) without any presence of corrugation or surface irregularities. As a polycrystalline surface, the Pd foil has grain domains whose boundaries can be visualized at the top right side of the picture. For the foil oxidized during reaction under excess O_2 (Fig. 3b), roughening on the surface can be seen. An even greater roughening of the surface is observed for the sample oxidized during reaction under excess methane (Fig. 3c). An increase of the surface area should be expected for samples b and c as compared to sample a, and this could possibly be the reason for the higher nominal turnover rates on the foil after activation.

To measure the surface area, a surface exchange experiment using $^{18}O_2$ was performed. Note that the total sample surface area is too small to be measured by a standard method (e.g., BET). The conditions of the isotope exchange for this work were devised using the values for the rate of oxygen exchange measured by Au-Yeung *et al.* (11) on zirconia-supported PdO catalysts. On the basis of this

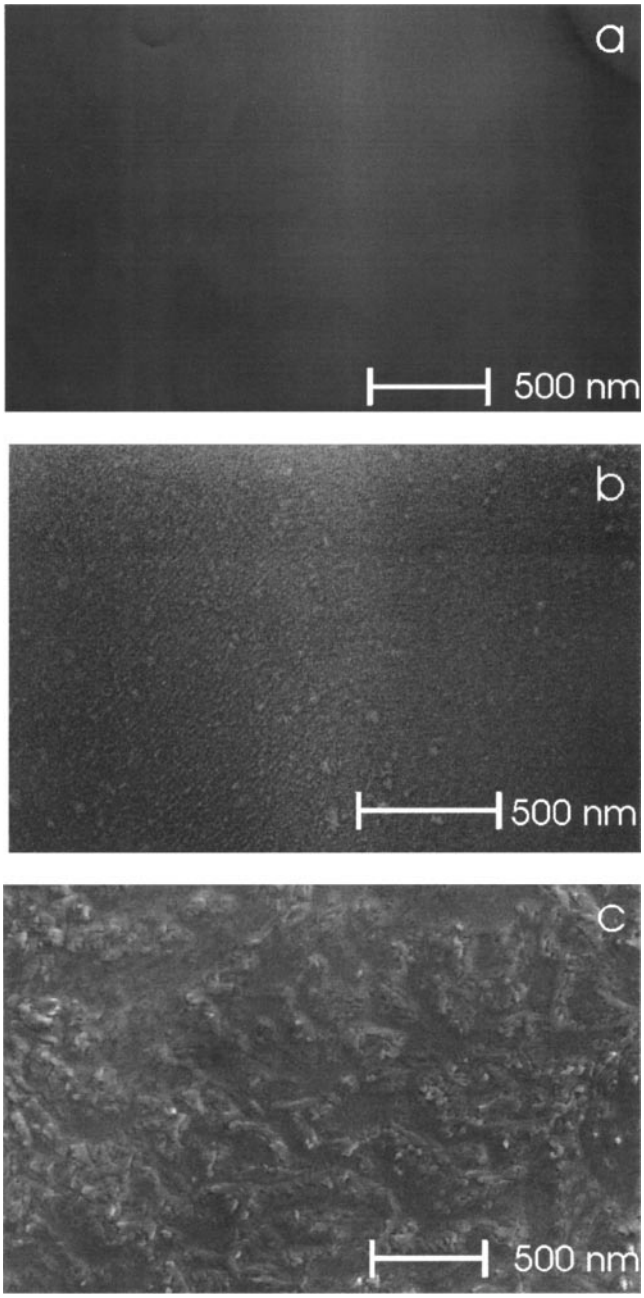

FIG. 3. SEM images for (a) clean Pd foil, (b) Pd foil after reaction in excess O_2 (598 K, 160 Torr O_2, 16 Torr CH_4, N_2 balance to 800 Torr, for 170 min), and (c) Pd foil after activation treatment (598 K, 16–4 Torr O_2, 160 Torr CH_4, N_2 balance to 800 Torr, for 60 min).

experiment and the measurement of the rate of oxygen diffusion into the bulk (6), we chose a condition that would guarantee surface exchange but negligible diffusion into the bulk. The procedure was to expose the sample to 5 Torr $^{18}O_2$ at 598 K for 12 s. Under these conditions, the rate of diffusion of oxygen into the foil is less than one layer of oxygen and the rate of exchange of surface oxygen is about 50 turnovers per site during the duration of the experiment. These calculations suggest that the exchange between ^{16}O in PdO and $^{18}O_2$ in the gas phase may be limited to the surface. Thus, the exchange of ^{18}O can be used as an absolute measurement of surface area. Even if our estimations are not correct and some bulk oxygen is also exchanged, this method can still be used as a precise relative measurement of the surface area among different samples, provided the numbers of layers of PdO are similar on the samples. The exchange results were measured by performing a TPD on the samples after reaction and the results are shown in Table 3.

To validate the method for the measurement of PdO area, another procedure to measure the surface area was carried out in the UHV chamber at a lower pressure of $^{18}O_2$. After the reaction at high pressure, the sample was transferred to the UHV chamber and prior to the isotope exchange, the sample was exposed to 5×10^{-4} Torr of nonlabeled O_2 at 500 K for 1 min, which eliminated the carbon-containing compounds present on the surface and which come from impurities present in the reaction cell. The XPS spectra showed the presence of PdO (BE = 336.8 eV) and no traces of carbon were detected after this procedure. The isotope exchange experiment was then carried out and it consisted of exposing the sample to 5×10^{-4} Torr $^{18}O_2$ at 598 K for 12 s. A TPD was then carried out to measure the amount of oxygen exchanged. The value for the number of ^{18}O layers exchanged after lean reaction was 1.8 (compared with 2 monolayers (ML) in Table 3) and 23 after exchange on a sample activated under excess methane (compared with 38 ML in Table 3). This result confirms the general procedure of using ^{18}O exchange to measure the PdO surface area.

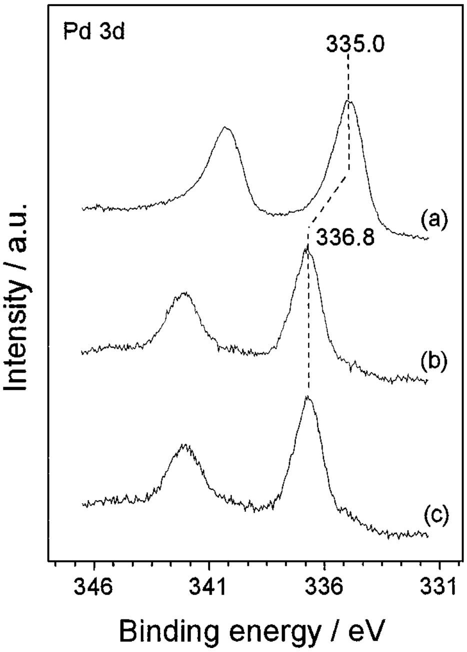

FIG. 4. Pd 3*d* core level XPS spectra for the Pd foil: (a) clean, (b) after reaction in excess O_2, and (c) after activation treatment. Same reaction and treatment conditions as in Fig. 3.

With the value of the surface area, the nominal TOR based on the initial geometric area can be transformed into the TOR based on the PdO area (Table 3). The reaction data refer to the sample after reaction in excess O_2 (not activated), after activation (batch 1, in Fig. 1), and after activation following one reaction in excess O_2 (batch 2, in Fig. 1). The $^{18}O_2$ exchange experiment measured the area for these three samples. The results show that the higher nominal rates for methane oxidation are related to the higher area of PdO, so the turnover rate per unit of PdO surface area did not change appreciably. For the sample corresponding to batch 2, the agreement was within a factor of 2, which reflects the experimental error of this method.

TABLE 3

Rates and PdO Surface Area for a Pd Foil after Various Treatments

Treatment before reaction	^{18}O exchange[a] (ML)	Nominal TOR[b] (10^{-2} s^{-1})	TOR[c] (10^{-2} s^{-1})
None	2	59	30
Excess methane(batch 1)	38	1188	31
Excess methane followed by reaction in excess O_2 (batch 2)	11	637	58

[a] Exchange carried out at 5 Torr $^{18}O_2$, 598 K for 12 s.

[b] Rates corrected for 550 K, 160 Torr O_2, 16 Torr CH_4, 1 Torr H_2O, N_2 balance to 800 Torr. Number of Pd sites was not measured but assumed constant and calculated from the initial geometric surface area for the clean foil.

[c] Number of sites was measured and based on PdO surface area before reaction.

3.3. Probing the Foil Surface before and after Reaction

The techniques of XPS and TPD were used to examine the state of the Pd foil surface after reaction in excess methane (sample activation) or O_2 (reaction probe). The Pd 3*d* core level of the XPS spectra in Fig. 4 shows that the binding energy of 335.0 eV, assigned to metallic Pd for a clean foil before reaction (Fig. 4a), shifted to a higher binding energy value of 336.8 eV, which corresponds to PdO, after reaction in excess O_2 (Fig. 4b). The same shift to higher binding energy of palladium was also observed after the pretreatment in excess methane (Fig. 4c). These values are consistent with the ones observed in the literature (12). On both surfaces, the oxygen-to-palladium atomic ratio as

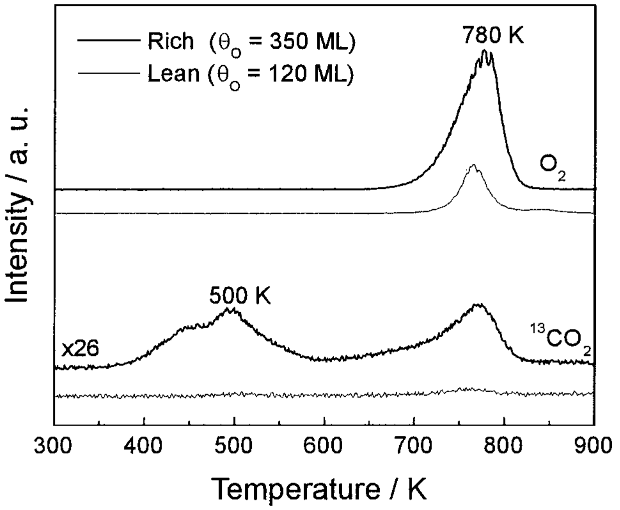

FIG. 5. TPD profiles after reaction in excess methane or O_2 on a Pd foil (same reaction and treatment conditions as in Fig. 3). The number of layers of oxygen desorbed are also given (θ_O).

measured by XPS was close to unity, which indicates the formation of palladium oxide (PdO). Thus, PdO is formed even under reaction conditions of excess methane. The XPS also shows a carbon-to-palladium atomic ratio around unity for both samples. This carbon signal was attributed to the presence of a carbon-containing impurity in the reactor cell that binds to the catalyst surface when the reactor is cooled and evacuated, as already discussed elsewhere (6). However, carbon from the activation treatment in excess methane is also on the surface and in the bulk of the sample.

The quantification of the amount of oxygen and carbon on the foil surface after reaction was also measured by TPD analysis. Labeled methane ($^{13}CH_4$) was used as a reactant to avoid interference from carbon-containing impurities present in the reaction cell. Under reaction conditions of excess methane or O_2, the TPD results in Fig. 5 show that the O_2 that originated from PdO decomposition reached a maximum at 780 K. However, the O_2 desorption signal after excess methane treatment was much more intense, which reveals that a larger amount of oxygen was incorporated into this sample. The amount of O_2 released after 170 min reaction in excess O_2 is 120 layers of oxygen (atomic oxygen) and after activation in excess methane for 60 min is 350 layers of oxygen. Thus, more oxygen was added in less time to the Pd foil activated under excess methane. Note that this higher uptake is not necessarily due to a deeper oxidation under excess methane. The unit used for the uptake of oxygen in "equivalent layers of oxygen" refers to the numbers of layers based on the initial area of the clean foil. If the surface roughens and its area increases, as it does in this case, oxygen will have more access points to reach the bulk and the uptake will increase although the thickness of the oxide layer may not change much.

For the quantification of carbon, no $^{13}CO_2$ was observed after reaction in excess O_2, which implies that the amount of carbon deposited on the surface during reaction under lean conditions is less than 5% of a monolayer, the sensitivity limit of the equipment. The results are quite different after reaction in excess methane. The presence of a low-temperature peak of $^{13}CO_2$ in the sample treated under excess methane is attributed to the oxidation of carbon deposited on the surface of PdO. The carbon dioxide peak at high temperature is located at the temperature associated with the large release of O_2 (PdO decomposition), which indicates that some carbon is incorporated in the bulk structure of the palladium oxide. The amount of carbon can be calculated from the amount of carbon dioxide released; in the bulk, the ratio of carbon to PdO is 0.03 (assuming uniform distribution) and on the surface, the ratio of carbon to PdO is 0.5.

3.4. Reaction Kinetics under Excess Methane

Kinetic studies under excess methane were performed but since the PdO surface area may change as a function of time of reaction, the results are difficult to interpret unless we had measured the surface area and shown that it did not change during the experiments. The invariance of the surface area in our case could not be assumed since the O_2 concentration varied substantially during the batch reaction experiments and it was shown that the sample surface area was a function of the O_2 partial pressure. Some of the experiments, however, can provide useful insights. The accumulation plots for the batch reactor were always straight lines passing through the origin even when the O_2 concentration decreased by 80% at the end of the reaction (Fig. 6). In these experiments, the methane concentration remained essentially constant but the O_2 concentration

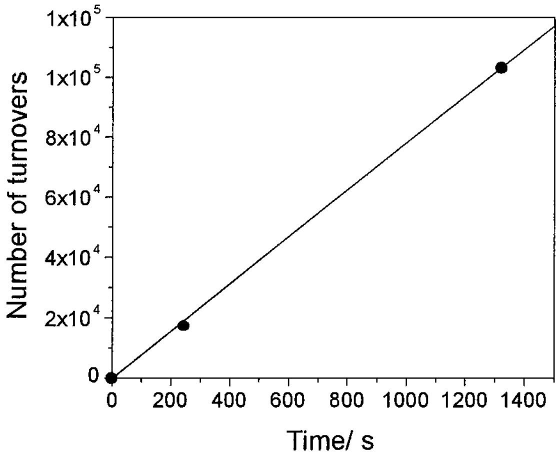

FIG. 6. Number of turnovers (CH_4 molecules converted per surface Pd atom) as a function of time for a reaction in excess methane. Initial reaction conditions were 598 K, 16 Torr O_2, 160 Torr CH_4, N_2 balance to 800 Torr. Amount of O_2 converted was 75%.

decreased and the H_2O concentration increased substantially as a function of time of reaction. The linear dependence of reaction product concentration with time is quite distinct from the results of a reaction under excess O_2 where the increase in H_2O concentration would have caused the rate to decrease as a function of time as in Fig. 2A. The order dependence in CH_4 was evaluated from 40–160 Torr CH_4, 16 Torr O_2, N_2 balance to 800 Torr and was found to be about zero order.

4. DISCUSSION

The influence of reaction conditions on the surface properties of palladium oxide has been studied in the literature (3, 5, 13–15). Konig *et al.* (3) and Graham *et al.* (5) carried out *in situ* spectroscopic ellipsometry experiments to monitor PdO formation on the surface of a Pd film, about 1 μm thick, during the oxidation of either carbon monoxide or methane. Their data showed that a porous PdO layer formed under reaction conditions of excess methane at 773 K. The estimated porosity was as high as 80%, which supported a significant increase in the surface area of the catalyst. Conversely, dense and smooth PdO layers were formed when the Pd film was treated in excess O_2. These results are in agreement with the data obtained in our work. We were able to show that although the Pd surface area increases, the turnover rate per unit of PdO surface area remained the same. Thus, we conclude that the rate of methane conversion is directly proportional to the PdO surface area.

It is reasonable to expect an increase in the roughness of the foil surface after oxidation since palladium oxide has a tetragonal structure (characteristic lengths $a = b = 0.3036$ nm; $c = 0.534$ nm (16)) with a palladium atom density which is 60% of the value for the palladium fcc metal (characteristic length $a = 0.38903$ nm (16)). Thus, the addition of oxygen to the foil is accompanied by volume changes that may explain the roughening of the surface. The SEM images (Figs. 3b and 3c) show significant differences of roughness between the samples. However, the mechanism through which the treatment in excess methane increases the PdO surface area much more than in excess O_2 is not known.

The relative partial pressure of O_2 and CH_4 seemed to play a role in increasing the surface area, since the magnitude of the foil activation was dependent on the amount of O_2 used in the treatment with excess methane. Indeed, the rate in excess O_2 (probe reaction) decreased by a factor of 4 when the initial amount of O_2 in the rich mixture increased from 16 to 48 Torr (Table 1). The TPD results in Fig. 5 showed that under treatment in excess methane, carbon is dissolved into the PdO bulk structure and thus carbon may play a role in the surface area increase by a factor of 38 as compared to the clean foil. In contrast, under reaction conditions in excess O_2, no carbon dissolution was observed by TPD (lower than the detection limit of 5% of a monolayer) and the surface area increased by a factor of only 2 as compared to that of the clean foil. The foil uptake in O_2 was also 3 times higher and happened in a third the time in excess methane than in excess O_2.

The dissolution of carbon in the bulk is a distinct difference for the sample treated in excess methane, and it may be related to the surface area increase. Carbon dissolution has been reported for Pd/C catalysts in a number of cases (17–20) and attributed to the presence of interstitial carbon atoms in the Pd lattice. However, the compound of interest is PdO, not Pd. On PdO, Haack and Otto (12) reported, on the basis of XPS data, that the amount of surface carbon on a Pd foil after reaction is very small (C/Pd = 0.01) but their maximum ratio CH_4 to O_2 was 10 times lower than the one used here. Baldwin and Burch (13) have observed a remarkable activity enhancement in the catalytic combustion of methane on supported Pd catalysts and, after ruling out other possibilities such as particle size, elimination of impurities, and variation in the chemical state of the palladium particles, suggested that the increase in the activity might be related to changes in the morphology of the Pd crystallites due to carbon dissolution. We have shown that the rate per unit of PdO surface area does not change even when carbon is dissolved in the bulk. However, an apparent increase in the rate would indeed have been observed if the PdO surface area had not been measured. Attempts to use pure hydrocarbons like ethylene to induce carbon diffusion in the bulk of Pd followed by reaction of methane under excess O_2 did not increase the catalyst activity on a supported catalyst (7), maybe because an increase in surface area is observed only if excess hydrocarbon and O_2 are introduced together.

Another report in the literature of rate enhancement was for the oxidation of ethane by pretreatment under excess ethane described by Descorme *et al.* (4). The authors reported that when Pd foils were preactivated by reaction in excess ethane at 450°C, the catalytic combustion of ethane under excess O_2 on an activated foil increased permanently by a factor of 20 as compared to that on the untreated foil. This large increase in activity resembles the activation observed in this study, but we think there was no sample activation since the rate increase persisted even after the foil was cleaned (sputtered and annealed). The cleaning treatment would have erased any preferential surface rearrangement or surface area increase. Our explanation for their results is that the reaction under excess ethane oxidized the sample more efficiently (as also observed in our case) and helped to bring deactivating impurities to the surface that could then be removed permanently. From our own experience, the Pd foil will not reach steady-state activity until the sample is subjected to various reactions at high pressure. It will deactivate from impurities migrating from the bulk, as observed by XPS (6). Once these impurities are removed by sputtering, the foil will show a higher and steady rate.

Following the foil activation (Fig. 1), the sample showed a steady deactivation in subsequent batch reactions. The continuous drop of the nominal turnover rate is attributed to a decrease in surface area as shown in Table 3 for the first two batch reactions in Fig. 1. The data in Table 1 showed that when an activated foil is pretreated in an oxidizing mixture without methane, the addition of either 5 or 10 Torr H_2O caused a significant decrease in the foil activity, similar to the one observed after reaction. On the other hand, the oxidizing treatment in the presence of O_2 did not produce any sample deactivation, and the turnover rate was as high as the one obtained for the activated sample. This experiment also shows that impurities adsorbed between reaction batches can be ruled out as a possible cause of deactivation in Fig. 1. Thus, the decrease in surface area is associated with the presence of water. A change in surface area as an explanation for the rate increase is also consistent with sample regeneration (second curve in Fig. 1); a new treatment in excess methane regenerates the surface area and produces a sample with a nominal turnover rate that is actually slightly higher than the first one. The higher rate is due to the higher initial area of the sample before the second activation as compared to the area of the fresh foil in the first treatment (factor of 6).

Water inhibited but did not deactivate the sample during the batch reactions, since the integrated forms of the rate equation in Fig. 2B are straight lines. It is counterintuitive that the sintering occurs when the sample is cooled. Most of the sintering mechanisms occur when samples undergo high-temperature treatments, especially in a wet environment. The cause for the loss of surface area is not known.

The kinetics of the reaction under excess methane was determined but not presented because the concentration of O_2 varied significantly in the experiments in excess methane. This variation in O_2 concentration could have affected the PdO surface area. However, unless the increase in surface area exactly compensated for inhibition by water and depletion of the reactant O_2, the straight line on the accumulation plots (Fig. 6) suggests that H_2O does not inhibit the reaction under excess methane. This fact and the observed zero order in methane indicates that the kinetics and thus the reaction mechanism under excess methane are distinct from those under excess O_2. In particular, the comparison of turnover rates under these two different conditions cannot be made as the rate for the reaction under excess methane seems not to depend on H_2O concentration but the one in excess O_2 is strongly dependent on it (−1 reaction order): the ratio of the rate under excess O_2 and under excess CH_4 could have any value depending on the chosen value for the H_2O concentration for the comparison.

5. SUMMARY

The nominal turnover rate of a Pd foil in the complete oxidation of methane under excess O_2 was increased by a factor of 19 after treatment in excess methane. The cause for the rate increase is the creation of a PdO surface with a surface area 19 times higher than the one for a foil after reaction under excess O_2. An explanation for the area increase was not found. However, under excess methane, carbon dissolved in the bulk of PdO and the uptake of O_2 by the foil was much higher than that under excess O_2. The turnover rate based on the PdO surface area however was invariant. The extent of the foil activation on the pretreatment was influenced by the partial pressure of O_2. The turnover rate decreased by a factor of 3 for foils treated in a mixture in excess methane when the initial O_2 pressure increased from 16 to 48 Torr. The PdO surface area was decreased by water generated during reaction and that led to a continuous decrease of conversion in subsequent batches under excess O_2. The surface could be reactivated with a new pretreatment under excess methane, but the foil deactivated again in subsequent reactions. In conclusion, although the treatment in excess methane produces a highly desirable increase in the conversion of a Pd foil through an increase in the PdO surface area, the catalyst will lose its surface area by interaction with water. The treatment should work for a sample with a Pd particle size that is large enough to resemble a foil. The activation treatment was not performed for supported catalysts but may work for samples with large particle sizes.

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