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Effect of Catalyst Structure on Methane Oxidation over Palladium on Alumina

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A series of palladium on alumina catalysts were prepared and tested for methane oxidation at 300°C, 50 Torr methane, 110 Torr oxygen, 900 Torr helium, and conversions less than 2%. During the reaction the palladium particles are oxidized. The extent of oxidation increases with decreasing particle size and increasing number of crystal imperfections. Palladium oxidation breaks apart the crystals, so that all the oxide is exposed and participates in catalysis. Turnover rates for methane oxidation, based on the oxygen uptake at the temperature and oxygen pressure of the reaction, vary from 0.004 to 0.15 s^{-1}. Our results suggest that the palladium oxide dispersed over the alumina is much less active than the oxide dispersed over the surface of the palladium crystallites. Also, chlorine deposited during catalyst preparation may inhibit the rate of methane oxidation. © 1990 Academic Press, Inc.

INTRODUCTION

The catalytic oxidation of hydrocarbons is an important technology for reducing the emission of pollutants from fossil fuel combustion processes (*1–7*). In support of this technology, we have undertaken a study of the effect of the catalyst structure on the rate of methane oxidation over platinum and palladium. Our first report demonstrated that this reaction is structure sensitive (*8*). For a standard set of reaction conditions, in which oxygen was present in 5% excess, the turnover frequency varied by more than 5000 from the least active to the most active catalyst. The activities of the catalysts increased in the following order: dispersed phase of platinum < small particles of palladium < crystalline phase of platinum < large particles of palladium. The structure sensitivity was best explained by the different ways these surfaces bind oxygen and activate it toward reaction with methane.

We have also found that the stability of the metal crystallites in an oxidizing environment depends on the composition of the support. On high-surface-area γ-alumina, relatively high dispersions of palladium were maintained during heating for several hours in air at 900°C. Other supports were less effective anchors for the palladium crystallites.

In this paper, we examine further the effects of catalyst structure on the rate of methane oxidation over palladium on γ-alumina. A series of samples were prepared in which the metal dispersion varied from 3 to 81%. The amount of oxygen adsorbed at the temperature and oxygen pressure of the reaction on each catalyst sample was determined and compared to the turnover frequency for methane oxidation. In addition, the reactivity of the adsorbed oxygen was evaluated by temperature-programmed reaction with methane.

METHODS

The catalyst support used in this study was Degussa flame-synthesized aluminum oxide "C". Before deposition of the palla-

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dium, the alumina was calcined in air for 24 h at 1000°C. This treatment reduced the surface area to 83 m^2/g. The palladium was deposited by ion exchange of H_2PdCl_4 with the alumina at room temperature for 24 h. The H_2PdCl_4 was prepared by dissolving $PdCl_2$ in an HCl solution, evaporating the solution to dryness, and redissolving the resultant maroon crystals in distilled water. After adsorption of the metal chloride ion, the catalyst was slowly filtered and rinsed with distilled water, and then dried in air overnight at 105°C. Three separate exchanges were carried out, yielding 0.2, 0.46, and 2.3 wt% palladium. Each of these samples was divided into three batches which were separately calcined at 500, 700, and 900°C in air for 2 h. The metal weight loadings of the samples were determined by inductively coupled plasma emission spectroscopy after the high temperature oxidation.

Adsorption experiments were conducted in a volumetric chemisorption apparatus (*9*). From 1 to 3 g of catalyst, in the form of 32- to 60-mesh pellets, was placed in an evacuable glass cell. The catalyst was reduced in 200 cm^3/min hydrogen for 1 h at 300°C, and cooled to 21°C in 5×10^{-7} Torr vacuum (1 Torr = 133 N/m^2). The uptake of carbon monoxide was determined by recording an adsorption isotherm and back-extrapolating the linear part of the curve to zero pressure. The fraction of exposed palladium was calculated, assuming 1.06 carbon monoxide molecules are adsorbed per surface palladium atom (*10*).

It was noted that if the cycle of 300°C reduction and 21°C carbon monoxide adsorption was repeated, the second uptake would be less than the first. A similar phenomenon has been observed by other researchers (*11*, *12*). Most of the adsorption capacity could be restored by reoxidizing the catalyst in 200 cm^3/min oxygen for 1 h at 550°C, followed by reduction in 200 cm^3/min hydrogen for 1 h at 300°C. Thus, after the initial carbon monoxide adsorption, the samples were cycled two or more times between 550°C oxidation, 300°C reduction, and 21°C carbon monoxide adsorption. After several cycles the uptake of carbon monoxide remained constant.

Oxygen adsorption experiments were conducted on the catalysts following the cycling treatment. The uptake of oxygen on the surface of the metal particles was obtained by measuring the adsorption isotherm at 21°C. The uptake of oxygen under conditions close to those encountered during methane oxidation was determined as follows. The sample was reduced in hydrogen for 1 h at 300°C, and evacuated to 1×10^{-6} Torr over 15 min at 300°C. Next, 1.5×10^{-4} mole of oxygen was dosed into the cell. After 1 h had passed, more oxygen was introduced to increase the pressure to about 115 Torr. The sample was then allowed to equilibrate for 6 to 12 h at 300°C, during which time the pressure in the chamber decreased to 110 ± 2 Torr. Finally, the sample was cooled to 21°C and the pressure recorded again. The amount adsorbed was calculated by subtracting the moles of oxygen remaining in the chamber from those initially dosed in. This procedure assumes there was no exchange of oxygen between the catalyst and the gas upon cooling to 21°C.

The reactivity of the oxygen adsorbed at 21 and 300°C was investigated by temperature-programmed reaction with methane. Immediately after an oxygen adsorption experiment, the chemisorption cell was evacuated for 10 min to 5×10^{-7} Torr. Next, methane (2.93×10^{-5} mole) was introduced, and the cell heated at 5°C/min while recording the pressure and temperature at 5 or 10°C intervals. The reaction of methane with the adsorbed oxygen proceeded with the formation of an adsorbed intermediate. Thus, the reaction rate was calculated from the rate of decrease of the methane pressure with increasing temperature. Temperature gradients in the chamber were corrected for by conducting the same experiment on an alumina support and then subtracting the apparent adsorption on the support from the adsorption on the catalyst.

Infrared spectra of the catalysts were obtained during the temperature-programmed reaction of methane with adsorbed oxygen. A 0.1-g sample was pressed into a 13-mm-diameter wafer and placed in an evacuable, glass cell. The catalyst wafer was treated exactly as described above, exposed to the same moles of methane, and then heated at 5°C/min. Infrared spectra were recorded at 20°C intervals during heating. We used a Digilab FTS-40 spectrometer with DTGS detector at 4 cm^{-1} resolution and coadding 256 scans.

The method of measuring the rate of methane oxidation was described in Ref. (*8*). Briefly, the reactor consisted of about 0.1 g of catalyst pellets suspended in a 6.35-mm-o.d. quartz tube. The temperature of the catalyst was measured at the entrance to the catalyst bed. The reaction products were analyzed by gas chromatography, using a 1.83-m Carbosphere column and thermal conductivity detector. Carbon dioxide was the only product detected. Catalyst charged to the reactor was heated in 50 cm^3/min helium to 300°C, then reduced in 50 cm^3/min hydrogen for 1 h at 300°C. Next, the reaction was carried out at 300°C with a feed gas containing 50 Torr methane, 110 Torr oxygen, and 900 Torr helium. The reaction was run for about 7 h, during which time the rate usually attained a steady value. The amount of catalyst and the flow rate were adjusted to keep the conversion below 2%, thereby avoiding any mass or heat transport effect on the observed rate.

RESULTS

The properties of the palladium on alumina catalysts are summarized in Table 1. The palladium dispersion varies over a wide range for the group of samples. As expected, it decreases with the amount of metal deposited and the severity of the oxygen treatment. Comparison of the palladium dispersions determined from the carbon monoxide uptakes before and after several cycles of oxidation, reduction and adsorption reveals that the latter value generally falls within 20% of the former. However, sample 13a is an exception. On this catalyst, the amount of surface palladium increases by 50% during cycling. Shown in the last column of the table is the ratio of oxygen to carbon monoxide adsorbed on the catalysts at 21°C. This value is reasonably close to 1.0 for all the catalysts except 13a. Sample 13a adsorbs one-third as many oxygen atoms as carbon monoxide molecules.

TABLE 1

Properties of the Palladium Catalysts

Sample number	Oxidation temperature (°C)	Total Pd (wt%)	Pd dispersion[a] (%)		O/CO adsorbed (cycled)
			Initial	Cycled	
11b	700	0.20	81	70	1.10
11c	900	0.20	55	65	0.74
12a	500	0.46	35	—	—
12b	700	0.46	56	48	0.92
12c	900	0.46	18	14	1.10
13a	500	2.30	32	48	0.31
13b	700	2.30	10	11	1.10
13c	900	2.30	3	3	1.00

[a] Based on carbon monoxide uptake at 21°C. Initial: carbon monoxide uptake measured after first reduction. Cycled: carbon monoxide uptake measured after several cycles of 550°C oxidation, 300°C reduction and 21°C carbon monoxide adsorption.

The equilibrium uptake of oxygen at 300°C and 110 Torr of oxygen far exceeds that taken up at 21°C. This indicates that some of the bulk palladium is oxidized under these conditions. In Fig. 1, the fraction of the bulk palladium oxidized is plotted as a function of the initial dispersion. The fraction of the bulk oxidized is calculated using the formula

$$\text{bulk Pd oxidized} = \frac{2(O_2 \text{ uptake at } 300°\text{C}) - 2(O_2 \text{ uptake at } 21°\text{C})}{\text{total Pd} - 2(O_2 \text{ uptake at } 21°\text{C})}.$$

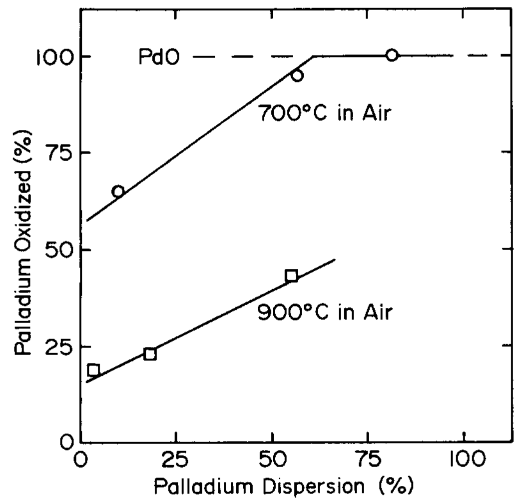

FIG. 1. Dependence of the fraction of palladium oxidized on the initial palladium dispersion and the temperature of prior calcination in air.

The data in the figure show that the amount of metal oxidized at 300°C is affected as much by the initial oxidation temperature as by the metal particle size. For samples previously calcined at 900°C in air, the amount oxidized increases from 21 to 43% as the palladium dispersion increases from 3 to 55%. Decreasing the calcination temperature from 900 to 700°C doubles the amount oxidized. Two of the samples previously calcined at 700°C, and having high dispersions, are completely converted to palladium oxide.

Shown in Fig. 2 are the spectra obtained for the temperature-programmed reaction of methane with oxygen adsorbed at 21°C. The peaks observed correspond to different reactivities of the methane with the adsorbed oxygen. Higher temperatures of maximum rate are indicative of higher activation energies of reaction. Approximately three peaks can be identified, with characteristic maxima at 135–155, 175–200, and 265°C.

In Fig. 2, samples 13a and 13b exhibit narrow, symmetric peaks, indicative of uniform reactivity of adsorbed oxygen with methane. The other samples show broad peaks with shoulders. The palladium particles on these samples contain adsorbed oxygen atoms which react at different rates with the methane. The temperature of maximum rate decreases on the series of catalysts in the following order: 13a < 11c < 12b = 12c = 13b < 13c = 11b.

Shown in Fig. 3 are the spectra obtained for the temperature-programmed reaction of methane with oxygen adsorbed at 300°C and 110 Torr of oxygen. Comparison of Fig. 3 with Fig. 2 reveals that the oxygen treatment at 300°C shifts the temperature of

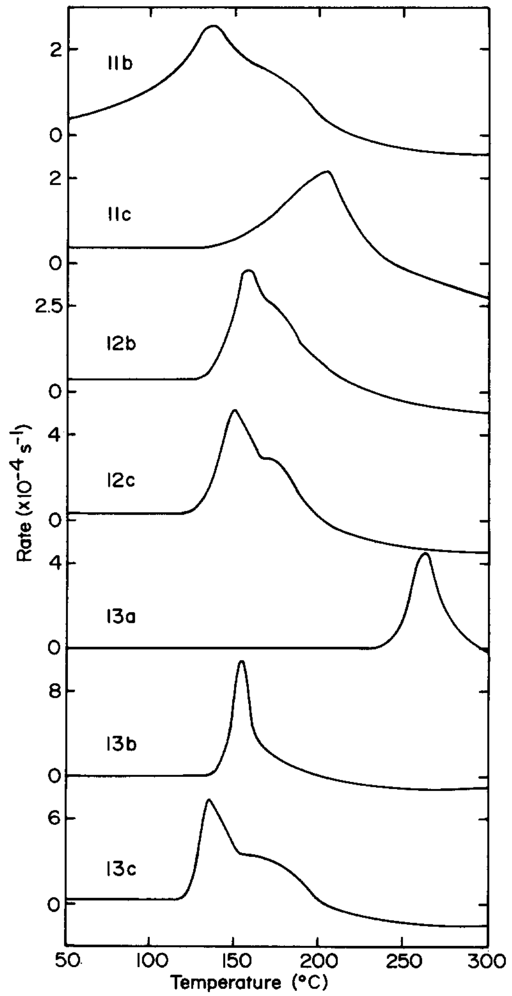

FIG. 2. Temperature-programmed reaction of methane with oxygen adsorbed at 21°C on the series of catalyst samples.

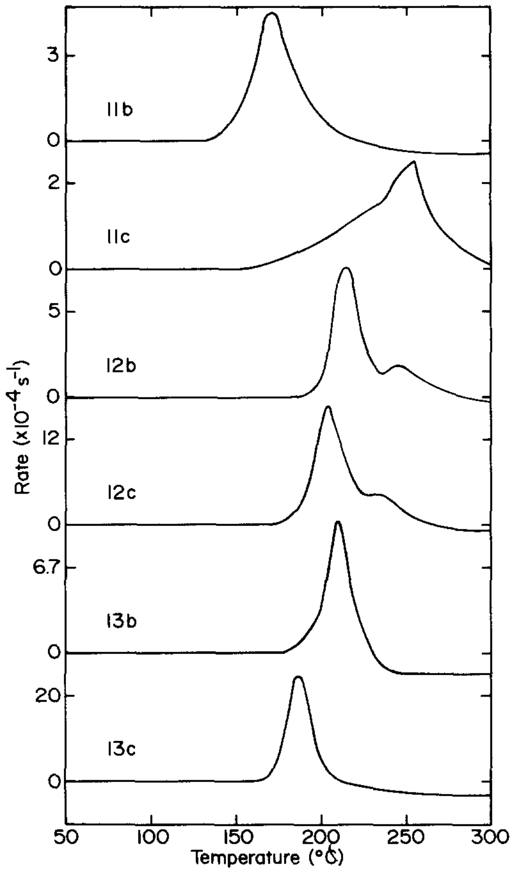

FIG. 3. Temperature-programmed reaction of methane with oxygen adsorbed at 300°C and 110 Torr of oxygen on the series of catalyst samples.

maximum rate upward by 35 to 55°C. It is also clear that the surfaces have become more homogeneous with respect to reaction with methane. This is particularly true for sample 11b which now shows only one symmetric peak in the spectrum. Nevertheless, the order of reactivity for the catalysts exposed to oxygen at 300°C has not changed relative to that observed for the catalysts exposed to oxygen at 21°C. The temperature of maximum rate on the series of samples decreases in the following order: 11c < 12b = 12c = 13b < 13c < 11b.

Table 2 lists the ratios of methane molecules converted per total adsorbed oxygen atoms during temperature-programmed reaction. Also shown are the temperatures of maximum rate for the most prominent peak in each spectrum. For both oxygen treatments, a stoichiometric conversion is observed of approximately 0.38 methane molecule per adsorbed oxygen atom. During the exposure to 110 Torr of oxygen at 300°C, oxygen reacts with the surface and the bulk palladium. Both of these types of adsorbed oxygen are included in the calculation of the methane reaction stoichiometry. The amount of oxygen reacted with the surface relative to the bulk at 300°C changes dramatically from sample to sample (see Fig. 1). In spite of this, the reaction stoichiometry remains the same, indicating that the oxygen adsorbed on the surface and by the bulk reacts quantitatively with the methane.

Shown in Fig. 4 are a series of infrared spectra of sample 13b during temperature-programmed reaction of methane with oxygen adsorbed at 21°C. Starting at 80°C, two bands appear at 1450 and 1650 cm^{-1}. These bands are due to carbonate adsorption on the alumina support (*13*). As the temperature is raised, the carbonate begins to desorb at 175°C. Then at 200°C, there appears a broad band at 1860 cm^{-1}, which is due to carbon monoxide adsorbed on the palladium. The carbon monoxide absor-

TABLE 2

Results of Temperature-Programmed Reaction of Methane with Adsorbed Oxygen

Sample number	O_2 adsorbed at 21°C		Equilibrated in 110 Torr O_2 at 300°C	
	CH_4/O_{ad}	T_{max}	CH_4/O_{ad}	T_{max}
11b	0.39	135	0.36	170
11c	0.42	200	0.37	250
12b	0.41	155	0.33[a]	215
12c	0.42	150	0.41	205
13a	0.40	260	—	—
13b	0.45	155	0.19[a]	210
13c	0.34	135	0.30	186

[a] Not enough methane was introduced into the cell to react with all the adsorbed oxygen.

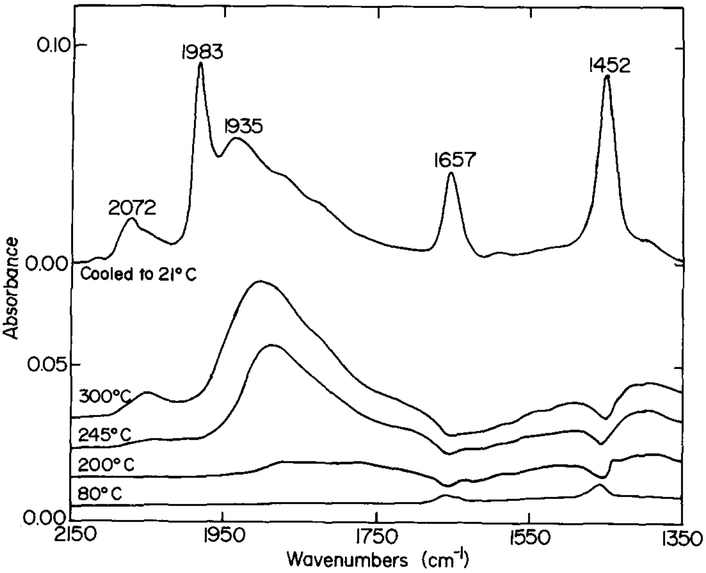

FIG. 4. Infrared spectra of sample 13b during temperature-programmed reaction of methane with oxygen adsorbed at 21°C.

bance grows in intensity as the temperature is raised, reaching a maximum value at 300°C. When the sample is cooled to room temperature, all the gas-phase carbon monoxide and carbon dioxide produced by the reaction are readsorbed. The infrared spectrum of the cooled sample shows the characteristic infrared bands for adsorbed carbon monoxide on palladium at 2072, 1983, and 1935 cm^{-1} and for adsorbed carbon dioxide on alumina at 1657 and 1452 cm^{-1}. Several other catalyst samples were characterized by infrared spectroscopy and showed the same behavior as sample 13b.

Examination of the temperature-programmed reaction spectrum of sample 13b (Fig. 2) reveals that the methane reaction is nearly complete at 175°C. At this point, the only reaction product observable in the infrared spectrum is carbon dioxide. Carbon monoxide is observed at higher temperatures. These results suggest that two consecutive reactions occur during heating. The first one is methane reaction with adsorbed oxygen to form adsorbed carbon dioxide. This reaction consumes all the oxygen and produces the peak in the temperature-programmed reaction spectrum. The second reaction forms adsorbed carbon monoxide. It proceeds slowly as the sample is heated from 200 to 300°C and causes a small increase in the chamber pressure. The pressure increase shows up as a slightly negative rate in the temperature-programmed reaction spectrum.

The rates of methane oxidation over the palladium on alumina catalysts are presented in Table 3. At the beginning of the reaction, the rate increases or decreases, depending on which catalyst is being tested. For sample 11c, the period of changing rate lasts 5 min. For samples 11b, 12b, 12c, and 13c, the period of changing rate lasts about an hour, while for sample 13b, it takes 4 h to attain a constant rate. Over samples 12a and 13a, the rates increase steadily throughout the 7-h run and show no signs of leveling off.

Presented in the last column of Table 3 are the turnover frequencies for methane oxidation. They are calculated by dividing the final rate by the initial palladium disper-

TABLE 3

Rates of Methane Oxidation over Palladium on Alumina[a]

Sample number	Initial dispersion (%)	Rate ($\times 10^{-4}$ mole/g Pd · s)		Final turnover rate[b] (s^{-1})
		Initial	Final	
11b	81	0.78	0.38	0.005
11c	55	4.40	0.88	0.017
12a	35	0.00	0.49[c]	0.015[c]
12b	56	0.00	0.63	0.012
12c	18	0.10	4.57	0.27
13a	32	0.00	1.26[c]	0.042[c]
13b	10	0.29	7.61	0.81
13c	3	0.10	1.55	0.55

[a] Reaction conditions: 300°C, 50 Torr methane, 110 Torr oxygen, 900 Torr helium, and conversions less than 2%.

[b] Turnover rate equals final rate divided by initial exposed palladium.

[c] Rate still increasing at end of 7-h run.

sion. A broad range of activities are exhibited by the catalysts. The turnover rates correlate with the temperature of initial oxidation of the catalysts and the size of the palladium crystallites. Samples 12a and 13a were the only samples oxidized at 500°C. They exhibit low turnover rates which steadily increase throughout the run. The other catalysts, oxidized at 700 and 900°C, show a trend of increasing activity with increasing particle size. Samples 11b, 11c, and 12b contain metal crystallites with greater than 50% of their atoms exposed, and their turnover rates average 0.01 s^{-1}. Conversely, samples 12c, 13b, and 13c contain metal crystallites with less than 20% of their atoms exposed, and their turnover rates average 0.5 s^{-1}. These results indicate that the rate of methane oxidation depends on the structure of the palladium surface.

DISCUSSION

Mechanism of Palladium Oxidation

At the temperature and oxygen pressure used in methane oxidation, a portion of the palladium crystallites oxidize. We now consider the mechanism of palladium oxidation and how this affects the structure of the catalytic surface.

Bayer and Wiedemann (*14*) investigated the oxidation of palladium powders by X-ray diffraction and thermal gravimetric analysis. During heating in air at 8°C/min, palladium oxidation started at 200°C and was not complete until 700°C. At about 900°C, the oxide rapidly decomposed back to palladium metal. The formation and dissociation of the oxides depended on the surface area and grain size of the metal powders.

Campbell *et al.* (*15*) examined the interaction of oxygen with polycrystalline palladium foils. The extent of oxidation of the foil was far less than that observed for the powders. At an oxygen pressure of 3.5×10^{-2} Torr and temperatures between 350 and 900°C, the foil adsorbed 345 monolayer equivalents of oxygen. The rate of adsorption, but not the total uptake, changed with temperature. After oxidation the surface of the foil was extremely rough and pitted. Campbell and co-workers found that the rate and extent of oxidation were strongly dependent on the source of the palladium foil and its treatment history.

Chen and Ruckenstein (*16–18*) and Jacobs and Schryvers (*19*) studied the reaction of oxygen with supported palladium crystallites by electron microscopy. They found that the metal particles became porous, and in many cases developed large pits, during oxidation. After being heated in air at 350°C, most of the particles retained their size, although some of the smallest ones broke apart and spread over the support. After being heated in air at 500°C, extensive fragmentation and spreading of all the particles were observed. Lattice imaging and optical diffraction showed that the oxidized particles contained mostly fcc metal (*19*). In very few instances was a lattice image attributable to crystalline palladium oxide observed.

Chen and Ruckenstein (*17*) proposed a mechanism of palladium oxidation which is consistent with the results presented above. The reaction is initiated at certain active sites on the metal surface. These sites may be lattice imperfections or step, corner, and edge atoms on the crystallites. As oxidation proceeds from these sites, cracks and fissures develop, exposing new surfaces which are oxidized. Once an oxide film has formed on all the surfaces, the reaction slows dramatically, because now oxygen must diffuse through the oxide film to react with the metal underneath. At 300 to 500°C, oxygen diffusion is probably so slow that none of the metal below the surface layer oxidizes. The metal particles obtained under these conditions are fragmented and porous, and consist of domains of fcc palladium metal covered over with a thin layer of oxide. This oxide covering would not be detectable by lattice imaging or optical diffraction.

Since the oxidation reaction requires special sites on the metal surface to occur, the extent of oxidation is sensitive to the structure of the palladium particles. In oxidation studies of the metal powders (*14*) and the metal foils (*15*), the sensitivity to structure is evidenced by the dependence of the reaction on the source of the material used and its treatment history. Furthermore, the reason that the foil oxidizes much less extensively than the powder, under similar conditions, is that the former exposes much less surface and far fewer crystal imperfections than the latter.

Our results further demonstrate the structure sensitivity of palladium oxidation. As shown in Fig. 1, the extent of oxidation depends on the particle size and the sample treatment history. The fraction of the bulk palladium oxidized increases with decreasing particle size (increasing dispersion). The effect of the prior calcination on the extent of oxidation can be explained as follows. Chen and Ruckenstein (*17*) have shown that cracked and pitted particles are obtained after heating to 700°C in air. However, during heating to 900°C in air, the oxide decomposes and the palladium agglomerates into uniform, highly ordered, metal crystallites. After reduction, the palladium particles calcined at 700°C will contain many more crystal imperfections than those calcined at 900°C. Thus, as is observed, the extent of reoxidation will be greater on the palladium initially oxidized at the lower temperature.

Sites for Methane Reaction

When the palladium is exposed to oxygen at 21°C, the oxygen adsorbs onto the surface of the particles and no further reaction takes place. Upon heating the catalyst in an atmosphere of methane, the surface oxygen is consumed with formation of adsorbed carbon dioxide and water. Further heating produces adsorbed carbon monoxide on the palladium. These reactions are documented by the infrared spectra recorded during temperature programming of sample 13b (Fig. 4). A reaction sequence consistent with these observations is

$$CH_4 + 4PdO_s \rightarrow 4Pd_s + CO_{2s} + 2H_2O_s \quad (1)$$

$$xCH_4 + Pd_s \rightleftharpoons PdC_{xs} + 2xH_2 \quad (2)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad (3)$$

$$CO + Pd_s \rightleftharpoons PdCO_s. \quad (4)$$

Our experiments and those of Frennet (*20*) indicate that methane will decompose to surface carbon and gaseous hydrogen on palladium at temperatures above 100°C. The reverse reaction, hydrogenation of adsorbed carbon, begins at about 215°C (*21*). The water-gas shift equilibrium constant, for the reaction as written above, is 0.026 at 300°C (*22*). This value is large enough for a significant amount of carbon monoxide to be formed from the carbon dioxide and hydrogen produced in the first and second reactions.

The observed reaction stoichiometry of about 0.4 (Table 2) can be explained by a carbon coverage (x) equal to 0.15 after heating the catalysts in methane. This coverage is in good agreement with the methane uptake measured by us in separate adsorption experiments. At 200°C, an oxygen-free palladium surface adsorbs on the average 0.1 methane molecule per exposed metal atom. At higher temperatures, the amount taken up increases slowly.

When the palladium is exposed to 110 Torr of oxygen at 300°C, the surface and some fraction of the bulk are oxidized. The data we have obtained indicate that methane reacts with all of the adsorbed oxygen, including that derived from the bulk. As shown in Table 2, the reaction stoichiometry is approximately the same for the oxygen treatments at 21 and 300°C. Furthermore, the stoichiometry does not change with each catalyst sample even though the ratio of surface to bulk palladium oxidized varies over a wide range. These observations support the proposal that bulk oxidation breaks apart the palladium particles, exposing the oxide at freshly made surfaces. The surface oxide created this way provides additional sites for methane oxidation.

Although we cannot provide a detailed interpretation of the temperature-programmed reaction spectra, several qualitative features of the methane reaction with the adsorbed oxygen are evident. Comparison of the spectra for the 300°C oxidized catalysts (Fig. 3) to the spectra for the catalysts exposed to oxygen at 21°C (Fig. 2) reveals the following: (1) the temperature of maximum rate is higher for the former than the latter; (2) except for sample 11c, the spectra observed for the 300°C oxidized samples contain one symmetric peak, indicating a uniform rate of reaction of methane with the adsorbed oxygen; and (3) the orders of reactivity exhibited by the series of catalyst samples are the same for both oxygen treatments. Observations 1 and 2 suggest that a uniform surface oxide is formed on the palladium particles at 300°C. The reactivity of this oxide is the same, whether it is formed on a preexisting surface or on one created by the oxidation reaction itself. Observation 3 suggests that some memory of the original palladium crystal structure is retained after the 300°C oxidation.

Structure Sensitivity of Methane Oxidation

If methane oxidation over palladium is carried out at temperatures between 200 and 900°C in an excess of oxygen, bulk oxidation of the palladium will occur. As discussed above, palladium oxidation creates new surfaces and new sites for the catalytic reaction. The inventory of active sites depends on the reaction conditions. An increase in the temperature or oxygen pressure during reaction may increase the inventory of active sites. Decreasing the temperature or oxygen pressure back to the original conditions may not recover the original activity of the catalyst.

In our experiments the catalysts are initially reduced, so the palladium undergoes oxidation upon introduction of the reaction mixture. As the metal oxidizes, new sites are created, and the rate of methane oxidation increases. Therefore, the period of changing rate exhibited by the catalysts at the beginning of the run may be due to palladium oxidation. Such a conclusion is supported by the correlation observed between the length of the period of changing rate and the rate of palladium oxidation. Sample 11c is oxidized nearly instantaneously upon exposure to 110 Torr of oxygen at 300°C, and this sample attains a steady reaction rate within 5 min. Conversely, sample 13b takes several hours to oxidize in 110 Torr of oxygen at 300°C, and it attains a steady reaction rate over a 4-h period. Samples 12b, 12c, and 13c take 1 h to oxidize and also exhibit 1-h periods of changing rate. On sample 13b, the palladium oxidation rate is slow because the metal particles are initially very large and they are extensively oxidized.

The effects of palladium oxidation on the palladium dispersion and the turnover frequency for methane oxidation are shown in Table 4. The final Pd dispersion is computed from the uptake of oxygen at 300°C and 110 Torr of oxygen, assuming O/Pd_s = 1.0. Samples 12a and 13a are not shown

TABLE 4

Comparison of the Extent of Palladium Oxidation with the Turnover Frequency for Methane Oxidation[a]

Sample number	Initial dispersion (%)	Bulk Pd oxidized (%)	Final dispersion[b] (%)	Final turnover rate[b] (s^{-1})
11b	81	100	100	0.004
11c	55	43	70	0.013
12b	56	95	97	0.007
12c	18	23	33	0.15
13b	10	65	68	0.12
13c	3	19	21	0.08

[a] Reaction conditions: steady state, 300°C, 50 Torr methane, 110 Torr oxygen, 900 Torr helium, and conversions less than 2%.

[b] Based on total oxygen uptake at 300°C and 110 Torr of oxygen.

because they do not exhibit steady reaction rates during the run. Their behavior is discussed later. The turnover rates presented in Table 4 vary from 0.004 to 0.15 s^{-1}. This range is narrower than that obtained when the turnover rates are based on the initial Pd dispersion (see Table 3). However, the variation is still large, indicating that the intrinsic activity is sensitive to the structure of the metal surface.

The steady state activities correlate with the extent of palladium oxidation. Samples 11b and 12b are completely oxidized and exhibit low turnover rates. By contrast, samples 12c, 13b, and 13c are partially oxidized and exhibit high turnover rates. The difference in activity may be related to the types of surface oxide formed on these catalysts during reaction. Samples 11b and 12b start out as small metal particles (high dispersion), which contain many crystal imperfections (700°C prior oxidation). When they are exposed to reaction conditions, they fall apart and disperse over the alumina as a layer of palladium oxide. On the other hand, samples 12c, 13b, and 13c start out as large metal particles (low dispersion). When they are exposed to reaction conditions, they break apart into smaller crystallites with a covering of oxide. Consistent with the trend observed, the palladium oxide dispersed over the alumina is much less active than the oxide dispersed over the surface of the fcc palladium crystallites.

One catalyst which shows anomalous behavior is sample 11c. This sample is relatively inactive, yet is partially oxidized under reaction conditions. Sample 11c may also be distinguished from the others in that it is rapidly oxidized upon exposure to 110 Torr of oxygen at 300°C. Moreover, it exhibits a short 5-min period of changing rate, in which the rate drops to one-fifth the original value. There are several possible explanations for the low activity of sample 11c. The palladium crystallites obtained after the initial 900°C calcination are small, i.e., 55% exposed. These small crystallites may strongly interact with the alumina. Oxidation does not seem to break up the particles, because the oxidation time is much shorter than that observed for other samples. Thus, the oxide formed on these metal particles may be stabilized by the alumina and show low activity for methane oxidation. Another possibility is that sample 11c contains two oxides: one spread over the alumina and one spread over the palladium crystallites. Since most of the oxide is of the former type, the intrinsic activity is low. A third possibility is that the catalyst may be poisoned by carbon deposition during the first few minutes of reaction. However, no other evidence was obtained to corroborate carbon poisoning.

Another discrepancy in the experimental results is the absence of a correlation of the temperature-programmed reaction spectra with the steady state turnover frequencies. The temperature of maximum rate in the spectra should provide an indication of the reactivity of the surface oxide. However, comparison of the temperature of maximum rate (see last column of Table 2) with the turnover rates (see Table 4) shows no trend. For example, samples 11b and 13c both have low temperatures of maximum rate, but their activities for methane oxidation are on opposite ends of the scale. These results may mean that the surfaces present during steady state methane oxidation are quite different from those on which the temperature-programmed reaction is carried out. Further studies are now underway to characterize the catalysts *in situ* during methane oxidation.

In summary, the turnover frequency for methane oxidation depends on the structure of the oxidized palladium surface present under reaction conditions. The palladium oxide distributed over the alumina appears to be less active than the oxide distributed over the fcc palladium crystallites. However, more experiments are needed to characterize the surface oxides and their individual contributions to the rate during steady state methane oxidation.

Lastly, samples 12a and 13a need to be considered. These catalysts exhibit low turnover rates that steadily increase throughout the run. This unusual behavior may be caused by chlorine poisoning. Samples 12a and 13a were prepared by impregnation of H_2PdCl_4 and oxidation in air at 500°C. When platinum on alumina catalysts are prepared by impregnation of H_2PtCl_6 and oxidation in air at 500°C, a "stable platinum oxychloride" forms (*23*). A similar palladium oxide–chloride species may form on the palladium on alumina catalysts. Other evidence for chlorine poisoning is the reduced oxygen adsorption capacity (low O/CO adsorbed for sample 13a, Table 1) and the reduced reactivity of the adsorbed oxygen with methane (high $T_{\max}$ for sample 13a, Table 2). Cullis and Willatt (*24*) have shown that the rate of methane oxidation over palladium on alumina is inhibited by chlorine. Thus, the slow steady increase in the methane oxidation rate during the run may result from the slow decomposition of an inactive palladium oxide–chloride species into an active palladium oxide species.

CONCLUSIONS

Supported palladium crystallites oxidize when methane oxidation is carried out in excess air. Oxidation breaks up the palladium particles into smaller pieces, with each piece being coated by a layer of oxide. The extent of palladium oxidation increases with decreasing crystallite size and increasing number of facets, twins, and other lattice dislocations. The crystal quality is strongly affected by the cycle of oxygen and hydrogen treatments prior to use. All of the oxide generated is exposed on surfaces and participates in methane oxidation. Thus, the extent of palladium oxidation during reaction determines the number of catalytic sites.

Turnover rates for methane oxidation, based on the number of oxygen atoms adsorbed at the temperature and oxygen pressure of the reaction, vary by 40-fold over the different catalyst samples. This suggests that the reaction rate depends on the structure of the oxidized palladium surface. One possible explanation of the structure sensitivity is that the oxide layer dispersed over the palladium crystallites is much more active than the palladium oxide dispersed over the alumina. The reaction also appears to be poisoned by chlorine remaining on the catalyst after preparation. However, both of these effects need to be verified by further experimentation.

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