JOURNAL OF CATALYSIS **146**, 537–544 (1994)

Kinetics of the Complete Oxidation of Methane over Supported Palladium Catalysts

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Received September 3, 1993; revised November 30, 1993

The complete oxidation of methane by supported Pd was studied in a reaction mixture of 2% CH_4 in air at 550 K, and atmospheric pressure. The catalysts were Pd supported on Al_2O_3 and ZrO_2 deposited from $PdCl_2$ or $Pd(NH_3)_2(NO_2)_2$ precursors. For the determination of how the turnover rate varies with the structure of the catalyst, the average Pd particle size on the series of catalysts was varied in the critical size range (1–10 nm). The number of active sites were measured before and after reaction by the method of H_2 titration of adsorbed oxygen at 373 K. The number of active sites remained the same, although the rate per gram of catalyst increased with time on stream for all catalysts. At steady-state, the turnover rate for the series of catalysts tested varied in the range 2×10^{-2} to 8×10^{-2} s^{-1} under the conditions of these experiments. It is concluded that the reaction is structure insensitive. In an investigation of the kinetics of methane oxidation on palladium, the reaction products were found to strongly inhibit the oxidation of methane.

1. INTRODUCTION

There are large world reserves of methane in the form of natural gas. Its utilization as an energy source is attractive because it has the highest ratio of hydrogen to carbon for a hydrocarbon and the levels of sulfur- and nitrogen-containing impurities are very low. To completely oxidize methane without the concurrent formation of high levels of NO_x, catalytic combustion is the most attractive choice (1). For catalytic combustion, Pd is one of the most active catalysts (2). Thus, it is important to understand the catalytic chemistry of CH_4 oxidation over supported Pd, and in particular how the turnover rate (TOR) varies with the structure of the catalyst.

Although the complete oxidation of CH_4 has been studied for many years (2–4), it is not clear if this reaction is structure sensitive. Cullis and Willat (3) found that the reaction is independent of the particle size, and Baldwin and Burch (5) found a change in TOR of two orders of magnitude on a series of catalysts with no correlation between particle size and TOR, while Hicks *et al.* (6, 7) found that the TOR is higher for larger Pd particles. The interpretation of the rate data is further complicated by the unusual behavior of the supported Pd system. For instance, on some of the catalysts the initial rate per gram steadily increased to many times the initial rate over a period of many hours (hundreds of turnovers) (5–7), a phenomenon which is not understood. Some catalysts have also shown a reversible deactivation dependent on the reaction temperature (8) or the fuel-to-air ratio (9).

Supported Pd catalysts present an unusual situation in that the thermodynamically stable phase can be either Pd metal or PdO, depending on the oxygen partial pressure and the temperature. In air at atmospheric pressure, the stable phase is PdO at temperatures below 1052 K, while metallic Pd is stable above 1052 K (10). In addition, significant work on the interaction of Pd with support surfaces demonstrates that in O_2 at temperatures in the range 870 to 970 K, PdO wets and spreads on oxide surfaces such as silica and alumina (11–14). Clearly, the heat treatment history can influence the bulk state and the percentage of metal exposed of the catalyst sample.

The many open questions for the oxidation of methane over supported Pd catalysts prompted this study of the turnover rate of methane oxidation over Pd. In the process of measuring the rates, it was found that the reaction products, H_2O and CO_2, significantly inhibit the reaction rate. This strong inhibition makes the measurement of specific rate difficult and could have an impact on the performance of practical catalysts. The activation of the catalysts under reaction conditions was also confirmed; the rate per gram of catalyst changes, but the Pd metal surface area remains constant. This activation process was studied to obtain a reproducible and constant steady-state rate to allow comparison of rates among different catalysts.

2. EXPERIMENTAL METHODS

All the catalysts were prepared by incipient wetness using aqueous solutions of the salts $Pd(NH_3)_2(NO_2)_2$ in nitric acid obtained from Tanaka Kikinzoku Kogyo of

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0021-9517/94 $6.00

Japan or $PdCl_2$ from Aldrich Chemicals. The $PdCl_2$ solution was prepared by the addition of 2 mol of HCl per mol of salt with a slight heating to help dissolution. The desired solution concentration was adjusted by the addition of distilled water.

The supports used were alumina V-GH from La Roche Chemicals, silica stabilized Al_2O_3 SR-II (Si-Al_2O_3) from W.R. Grace, and zirconia RC-100P from Daichi Kigenso Kagaku (DKK) of Japan. The supports were further calcined in a muffle furnace in laboratory air for 10 h. The data on calcination temperature, surface area for the support, Pd precursor, and final calcination conditions used for the various catalysts are collected in Table 1.

The chemisorption measurements were made according to the procedure of Benson *et al.* (15). The sample was reduced in 1 atm of H_2 at 373 K for 1 h, followed by evacuation at the same temperature for 1 h. O_2 was then introduced at a pressure of 240 Torr at 373 K for 1 h, followed by evacuation at the same temperature for 0.5 h. An adsorption isotherm at 373 K for H_2 was obtained with 6 points between 80 and 200 Torr. The H_2 uptake was obtained by extrapolation of the linear isotherm to zero pressure and the surface Pd calculated assuming the stoichiometry $PdO + \frac{3}{2}H_2 \rightarrow PdH + H_2O$. The crystallite size based on chemisorption measurements was estimated from the expression d(nm) = 112/(percentage of metal exposed). This expression assumes spherical particles and a Pd surface atom density equal to an average of the low index planes of 1.27×10^{19} atoms m^{-2} (16, 17).

The identification of solid-state phases and the measurement of Pd crystallite size by X-ray diffraction (XRD) were performed on a Scintag XDS 2000 run at 45 kV, 40 mA, with unfiltered radiation from a Cu target. The identification of crystalline phases present was done without further sample treatment. The crystallite size was determined on the reduced sample following chemisorption. The crystallite size was calculated by the Scherrer equation with the peak width determined through curve fitting on the Pd 111 reflection. The instrument broadening was determined with a Si sample from the National Institute of Standards and Technology (Si 640 B).

To evaluate the importance of the initial bulk state, the 8.5% Pd/Al_2O_3 and 10% Pd/ZrO_2 samples were prepared in both metallic (Pd) and oxide (PdO) form. The metallic Pd form was prepared by calcination at 1123 K in a muffle furnace in air for 24 h, conditions under which Pd is the stable phase. This sample was then quenched to low temperature by rapidly spreading the sample onto a glass container maintained at LN_2 temperature. A portion of this sample was subsequently treated at 973 K in air for 24 h, conditions under which PdO is the stable phase. X-ray diffraction measurements of these samples showed pure metallic Pd for the 1123 K quenched sample and pure PdO for the 973 K sample.

All the experiments for the measurement of rates and reaction orders were run at atmospheric pressure in a down flow, tubular, stainless-steel reactor of 0.95 cm internal diameter, and 71 cm total length. The tubular reactor was heated by a 60-cm-long cylindrical furnace providing a 10-cm zone with a uniform temperature. The catalyst (50–150 mg) was mixed with a quantity of the corresponding support (1–5 g), ground in a mortar, pressed into pellets, and sieved to 0.4–0.85 mm particles. The amount of support mixed with the catalyst was chosen to fill a 4–5-cm length in the catalyst bed. The amount of catalyst in each run was chosen to maintain a similar conversion at 550 K for all the runs.

The gases used were N_2 (Linde, prepurified), air (Linde, dry), 2% CH_4 balance air (Linde, certified custom grade), 2% CO_2 balance air (Linde, certified custom grade), ethylene (Scott, polymer grade), and CH_4 (Linde, CP grade). The gases were used with no further purification.

The reaction products were analyzed in a Hewlett–Packard 5880 gas chromatograph with a thermal conductivity detector. The products were separated on a 0.32 cm (1/8″)-diameter, 4.5-m packed column from Supelco (60/80 mesh Carboxen 1000), at 423 K with He as a carrier gas at a total flow of 100 cm^3 min^{-1}.

TABLE 1

Catalyst Preparation Parameters

	Support				Final calcination	
Catalyst	Support identification	Calcination temp. (K)	S_g (m^2 g^{-1})[a]	Pd precursor	Temp. (K)	Time (h)
8.5% Pd/Al_2O_3	La Roche V-GH	1123	~130	$PdCl_2$	1123	24
10% Pd/ZrO_2	DKK-RC-100P	1273	9	$Pd(NH_3)_2(NO_2)_2$	1123	24
1.0% Pd/ZrO_2	DKK-RC-100P	1123	23	$Pd(NH_3)_2(NO_2)_2$	1123	24
7.7% Pd/Si–Al_2O_3	Davison SRS-II	1323	140	$Pd(NH_3)_2(NO_2)_2$	773	10
0.77% Pd/Si–Al_2O_3	Davison SRS-II	1323	140	$Pd(NH_3)_2(NO_2)_2$	773	10

[a] Specific surface area after calcination for 10 h.

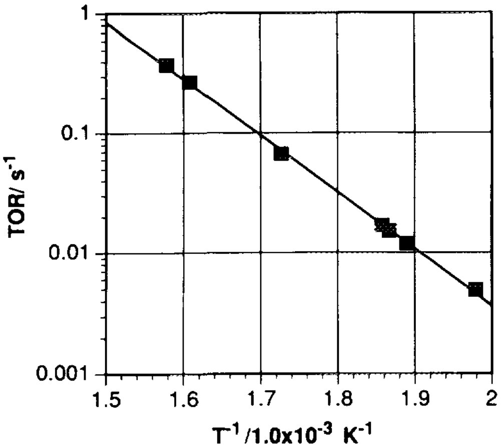

FIG. 1. Arrhenius plot for catalyst 0.77% Pd/Si–Al_2O_3 run in 2% CH_4/air.

The following procedure for measuring rates was used to obtain consistent results. The reactor was flushed with flowing N_2 for 1 h at room temperature. The temperature was then increased gradually over a period of 0.5 h under flowing N_2 until it stabilized at 550 K. The reaction was initiated by switching from the purge gas to a stream of 2% CH_4 in air at a flow rate of 189 cm^3 min^{-1}. The first analysis was made after 5 min (initial rate) and then at various intervals over a total reaction time of at least 24 h. The reaction temperature was then varied for the calculation of the apparent activation energy. A typical Arrhenius plot from which activation energies were calculated is shown in Fig. 1. After reaction, the sample was cooled in the reaction mixture to room temperature and exposed to laboratory air. Chemisorption measurements were made on the used catalysts, as previously described.

For the determination of the reaction order dependence on CO_2 and H_2O, additional amounts of CO_2 and H_2O in excess of reaction product concentrations were simultaneously added to the reaction feed. In this way, the product concentration variation throughout the bed was minimized. Streams of 2% CH_4/air, 2% CO_2/air, air, and H_2O vapor were mixed and added to the reactor inlet. The reaction rate dependence on CO_2 was measured at 1% CH_4, 0.046% H_2O, 0.012 to 0.82% CO_2, and balance air with a maximum conversion level of CH_4 of 2.5%. Similarly, the dependence on H_2O was measured at 1% CH_4, 0.03–0.15% H_2O, 0.24% CO_2, and balance air with a maximum conversion level of 3%. Water vapor was added to the gas stream by passing air through a water saturator in a constant temperature bath. The water vapor concentration in the reactant stream was adjusted by varying the fraction of air flowing through the saturator.

3. RESULTS AND DISCUSSION

The main objective of this paper is to report the measurement of turnover rates on supported Pd catalysts of varying crystallite size. First, it was necessary to prove that the reactions were run in the kinetic regime. Second, the discovery of inhibition by the reaction products required a quantification of this effect to ensure that rate measurement was done properly. Finally, the phenomenon of increasing rate with time on stream was explored.

3.1. Heat and Mass Transfer Limitations

The complete oxidation of methane is a highly exothermic reaction. To check for the absence of heat and mass transfer limitations, the Koros–Nowak test (18, 19) was employed. This test consists of running the reaction on at least two catalysts with different Pd loading but similar percentage of metal exposed (PME). The results are summarized in Table 2. The two catalysts in Table 2 have the same turnover rate, which indicates that there are no internal or external heat or mass transfer limitations in our rate measurements.

In the course of measuring the above rates, it was found out that the rate of CH_4 oxidation per g of catalyst did not stay constant as the reactant gas flow rate was varied (Fig. 2). At higher flows, when the conversion is lower, the rate per g of catalyst increased. The cause for this behavior, as will be discussed in the next section, is inhibi-

TABLE 2

Test for Heat and Mass Transfer Limitations

Catalyst	Rate (10^{-8} mol s^{-1} g^{-1})	TOR[a] (10^{-2} s^{-1})	Methane conversion (%)	PME[b] (%)	Crystallite size[c] (nm)
7.7% Pd/Si–Al_2O_3	220	1.7	1.60	18.1	6.2
0.77% Pd/Si–Al_2O_3	20	1.7	1.52	16.1	7.0

Note. Reaction run in 2% CH_4/air, 550 K.

[a] The number of active sites were counted after reaction by titration of adsorbed oxygen with H_2 at 373 K.

[b] Percentage of metal exposed.

[c] Crystallite size determined by d = 112/PME.

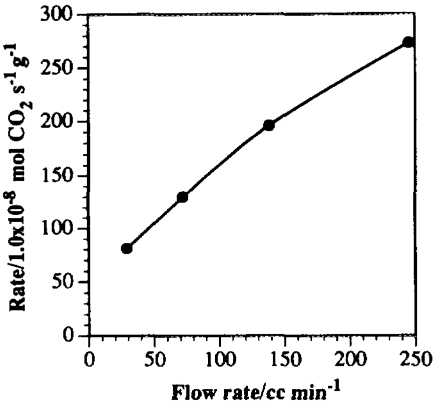

FIG. 2. Variation of the rate of methane oxidation with flow rate on 7.7% Pd/Si–Al_2O_3 run at 550 K in 2% CH_4/air.

tion by the reaction products on the rate of CH_4 oxidation. Due to this inhibition, activity comparisons between different catalysts must be done with care. At the minimum, the comparison must be done at the same conversion level (Table 2).

3.2. Determination of the Reaction Order on H_2O and CO_2

As noted above, product inhibition can severely influence differential rate measurements and complicate the comparison of different catalysts. As described in the experimental section, the reaction rate dependence on CO_2 was measured by establishing conditions of excess H_2O and varying the CO_2 concentration. Similarly, the dependence on H_2O was measured by establishing excess CO_2 and varying the H_2O concentration. The results are collected in Figs. 3 and 4.

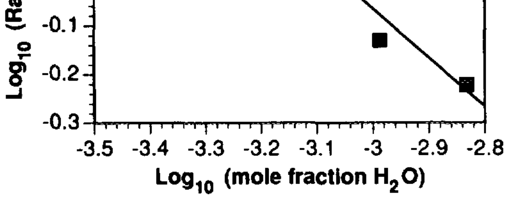

FIG. 3. Effect of added H_2O on the rate of methane oxidation over 7.7% Pd/Si–Al_2O_3. Reaction run at 550 K, with a feed of 1% CH_4, 0.25% CO_2, variable amounts of H_2O, and balance air. The H_2O concentration is the average between inlet and outlet concentration.

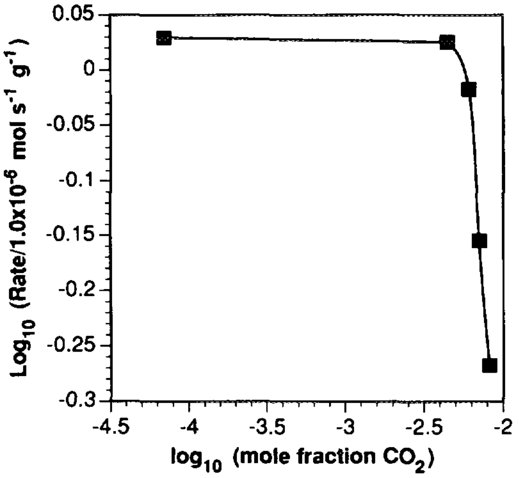

FIG. 4. Effect of added CO_2 on the rate of methane oxidation over 7.7% Pd/Si–Al_2O_3. Reaction run at 550 K, with a feed of 1% CH_4, 0.046% H_2O, variable amounts of CO_2, and balance air. The CO_2 concentration is the average between inlet and outlet concentration.

Water has a pronounced inhibiting effect on the rate, as shown in Fig. 3. An order dependence for H_2O of -0.98 was determined by linear regression of the data plotted in Fig. 3. The -1 reaction order for H_2O suggests that it competes effectively with CH_4 for surface sites under these reaction conditions. To understand this inhibition, it should first be noted that under the oxidizing reaction conditions of this work, the stable form of Pd is PdO. Cullis and Nevell (20) and Cullis *et al.* (21) also found water inhibition in their studies of CH_4 oxidation and they suggested that H_2O reacts with PdO to reversibly form $Pd(OH)_2$. Card *et al.* (22) showed in a TGA experiment that $Pd(OH)_2$ decomposes to PdO at about 520 K when heated in N_2 at 10 K min^{-1}. These results suggest that the strong inhibition by H_2O could be due to formation of $Pd(OH)_2$ at the PdO surface, effectively blocking access of CH_4 to the active PdO phase.

The inhibitory effect of CO_2 is more complex. Up to about 0.5% CO_2 by volume, no effect on reaction rate is observed. However, above this amount, the observed reaction order is -2 (Fig. 4). One relevant conclusion is that at the low conversion used in this study, which produces about 0.06% CO_2, the CO_2 generated by the reaction itself will not affect the rate measurements. At higher concentrations, CO_2 strongly inhibits the reaction rate. The surface chemistry of this inhibition is not understood.

3.3. Sample Activation

Observations of an increase in the rate per g of catalyst with time on stream of Pd (5–7, 23) and Pt (24) catalysts during the oxidation of methane have been reported in the literature. This type of rate increase was also observed for all the samples tested in this study. A typical plot of

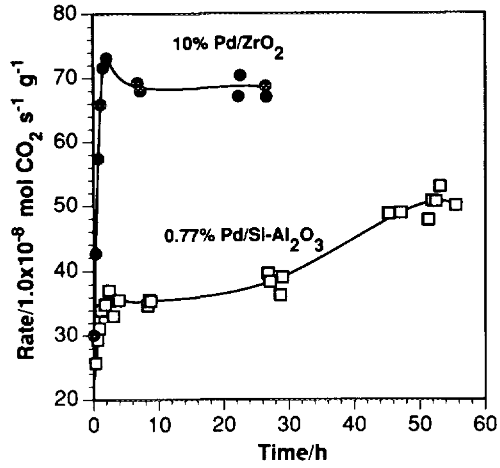

FIG. 5. Methane oxidation on 10% Pd/ZrO$_2$ (●) calcined at 973 K for 24 h and on 0.77% Pd/Si–Al$_2$O$_3$ (□). Run in 2% CH$_4$/air, at 550 K.

rate versus time on stream is shown in Fig. 5. The initial rate was measured after 5 min on stream (about 10 turnovers) and the steady-state rate was measured after about 24 h. All the samples tested exhibited a rate increase with time on stream with a steady-state rate about 2.5 times higher than the initial rate. Most of the rate increase occurred during the first 3 h of reaction and for the next 21 h, the rate per g of catalyst stayed constant or decreased slightly (20% from the maximum value). The only exception to this general behavior was the 0.77% Pd/Si–Al$_2$O$_3$ sample (Fig. 5).

Palladium site concentration (Pd$_s$) was measured before and after the rate measurements and was found to be relatively constant (Table 3). The titration procedure used to measure Pd site concentration employed a mild treatment procedure, reduction in H$_2$ at 373 K and oxidation in 240 Torr O$_2$ at 373 K, and is not expected to significantly alter the Pd percentage of metal exposed. For this reason, the titration measurement should quantify any changes in Pd dispersion caused by pretreatment or reaction. In addition, as shown in Table 3, calcination in air at 973 K resulted in a substantial redispersion of PdO from the 1123 K calcined and quenched state. This is a highly reversible process resulting in an increase in Pd$_s$ by a factor of 2.5. Both the dispersed PdO and the quenched metallic Pd samples showed similar rate increases during reaction. These results establish that the increase in reaction rate is not due to gross redispersion of the Pd during reaction. The same conclusion was reached in the work of Briot and Primet (23).

To understand this activation process, the 0.77% Pd/Si–Al$_2$O$_3$ sample was studied in more detail. This sample, previously calcined in an air muffle furnace at 973 K, was placed in the reactor and heated *in situ* in synthetic air at 550 K for 1 h. The temperature was reduced to 533 K and the CH$_4$/air reaction mixture flowed over the catalyst. The measured reaction rate was converted to a standard temperature of 550 K using the activation energy measured for this catalyst and reported in Table 3. The data are presented in Fig. 6. Note that although the conversion level and consequently the concentration of H$_2$O will vary as the temperature is changed, the inhibition by H$_2$O is included in the apparent activation energy (E_a) calculated at the end of the run. An example of rates measured over a wide concentration range can be seen in Fig. 1; the

TABLE 3

Kinetic, Chemisorption, and X-Ray Diffraction Data on Supported Pd Catalysts

Data set	Catalyst	Catalyst calcination temp. (K)	Rate[a] (10^{-8} mol s^{-1} g^{-1})	Pd$_s$[b] (μmol g^{-1})		TOR[c] (10^{-2} s^{-1})		Conversion[d] (%)	E_a (kJ mol^{-1})	Crystallite size[e] (nm)	
				Initial	Final	Initial	Final			By chem.	By XRD
1	8.5% Pd/Al$_2$O$_3$	973	50	18.3	19.3	—	2.6	1.3	76	49	19
2	8.5% Pd/Al$_2$O$_3$[f]	1123	50	6.7	6.0	5	8.3	0.8	76	134	120
3	10% Pd/ZrO$_2$	973	70	32	32	0.9	2.2	2.5	85	33	10
4	10% Pd/ZrO$_2$[g]	1123	53	13	12.3	1.7	4.3	1.3	78	81	45
5	1.0% Pd/ZrO$_2$	773	130	24.6	21.6	2.6	6.0	3.5	85	4.3	[h]
6	7.7% Pd/Si–Al$_2$O$_3$	773	260	131	119	1.2	2.2	1.7	85	6.2	4.5
7	0.77% Pd/Si–Al$_2$O$_3$	773	50	31	24	0.9	2.1	1.3	92	2.6	[h]

[a] Per g of catalyst, at 550 K, 2% CH$_4$/air.

[b] Number of Pd surface sites counted by H$_2$–O$_2$ titration at 373 K.

[c] Run at 550 K, 2% CH$_4$/air.

[d] Percent of CH$_4$ converted at steady state at 550 K.

[e] Crystallite size for the samples before reaction.

[f] Sample quenched after calcination.

[g] Sample quenched after calcination and reduced in H$_2$ at 373 K.

[h] Not detected.

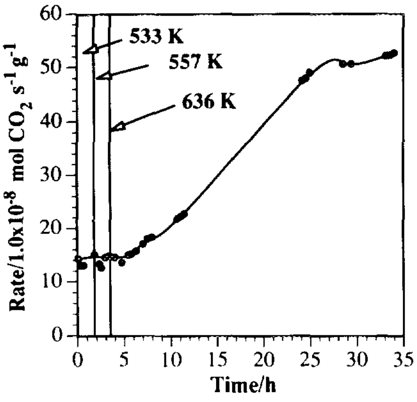

FIG. 6. Methane oxidation on 0.77% Pd/Si–Al_2O_3 run in 2% CH_4/air, at 550 K. Sample brought up to reaction temperature in flowing air. Rates reported at a higher temperature were recalculated at 550 K.

conversion level was varied from 0.3 to 23% with no deviation in linearity of the Arrhenius plot. In Fig. 6, the initial rate appeared stable for the first 4 h but the rate per g was substantially below the fully activated rate, as shown in Fig. 5. Increasing the reaction temperature to 557 K had no apparent effect, while at a temperature of 636 K, the sample began to show an increase in rate with a final rate close to that measured in the standard procedure (Fig. 5). Treatment *in situ* with air appears to make the catalyst more difficult to activate. This same effect on activation for an oxidizing treatment as compared to an inert gas treatment was reported by Cullis and Willat (3). Reduction in H_2 before reaction also had no effect on the activation, in agreement with the observations of Baldwin and Burch (5).

To test the effect of the presence of carbon on Pd as the cause of the observed rate increase with time on stream, the reaction on the 0.77% Pd/Si–Al_2O_3 sample was started in the usual way and after 6 h of reaction at 550 K, the catalyst was exposed to a reactant stream of 100% methane or 100% ethylene at 550 K for 20 min. The reactant mixture of CH_4/air was restarted after each treatment. A reaction exotherm was recorded after the ethylene treatment, but the reaction rate was the same before and after the treatment.

In summary, an *in situ* treatment in air, methane, or ethylene had no effect in the sample activation. The only effect observed (not shown here) was a temporary increase in the reaction rate for samples treated for prolonged periods of time in the presence of a dry gas. This increase in rate (about a factor of 2) was caused by the adsorption of the reaction product water by the support resulting in a decrease in water partial pressure over the catalyst and an increase in rate. This interpretation was confirmed by gas chromatographic analysis, which showed no H_2O in the reactor effluent during the period when the rate was high and the appearance of H_2O when the rate returned to its steady-state value.

The samples can only be activated under reaction conditions and at a high temperature. Measured percentage of metal exposed was the same before and after reaction rate measurements (Table 3) so that the observed increase in rate is not due to an increase in PdO surface area. A possible explanation is a change in morphology or surface reconstruction of the PdO under reaction conditions to yield a more active phase. This change cannot be measured by chemisorption because this technique is not sensitive to a morphology change as long as the exposed PdO remains constant.

The phenomenon of an increase in reaction rate with time on stream has been well documented in the literature. For the synthesis of NH_3, Fe crystallites reconstruct under reaction conditions to expose preferentially the more active 111 planes (25, 26). More relevant to our study is the example of NH_3 oxidation to NO on a Pt–Rh gauze, in which the reconstruction results in a substantial change in surface morphology (27). This reconstruction occurs under reaction conditions but not under either NH_3 or O_2 alone at reaction temperature. Another example is the CO oxidation catalyzed by Pt, for which the early work of Langmuir reported a rate increase under reaction conditions (28). More recent work on this subject has shown that the Pt(110) surfaces become more active during CO oxidation by the formation of microfacets, which have a higher specific activity. The Pt(110) changes its morphology during catalytic reaction but not when it is heated either in pure CO or in pure O_2 (29). These changes in morphology are usually accompanied by a modest change in the metal exposed area as compared to the changes in rates. Lee and Schmidt (30) found that the change in H_2 uptake on a Rh/SiO_2 sample induced by cycles of H_2 and O_2 treatments was only by a factor of 3, while the rate of ethane hydrogenolysis changed by a factor of 1000. In all these cases, the activity changes cannot be accounted for by the change in surface area. A similar process can be the cause of the rate increase observed in this work.

3.4. Dependence of Reaction Rate on Particle Size and Support

The turnover rates were measured on a series of Pd catalysts with different supports, Pd precursors, and Pd particle sizes (Table 3). The initial turnover rate reported in Table 3 was calculated after 5 min on stream (after 5–10 turnovers) and is based on the Pd surface area measured for the fresh sample. The turnover rate at steady-state (at least 24 h on stream) was calculated based on the Pd surface area after reaction.

The final turnover rate ranged from 2×10^{-2} s^{-1} to 8×10^{-2} s^{-1} when the particle size was varied between

2 and 110 nm. Thus, there is only a small change in the TOR when the support, Pd precursor, and Pd particle size are changed. For this reason it appears that the reaction is *structure insensitive*. Note that the measured values for the apparent activation energies also vary within a narrow range.

4. GENERAL DISCUSSION

Values of TOR for the oxidation of CH_4 reported in the literature are collected in Table 4. They were recalculated under the conditions of this work with the activation energies and reaction orders in O_2 and CH_4 given in the original publications. The reaction orders were assumed to be 0 and 1 for O_2 and CH_4, respectively, when the reaction order data was not available. No pulse reaction data was included because the samples would not have been able to activate under these conditions. No reaction data under overall reducing conditions were included because the active phase in this case would be Pd and not PdO; Pd might behave quite differently compared to PdO in the methane oxidation reaction.

The small difference in the turnover rate found here is to be contrasted with the wide variation reported in the literature (Table 4). Also, there is not an agreement for the dependence of the TOR with particle size; Hicks *et al.* (6, 7) reported that larger Pd particles have a higher TOR and Baldwin and Burch (5) reported a variation in the TOR but no correlation with the particle size, while Cullis and Willat (3) found that the TOR does not depend on the particle size. The major cause of the large variation in the literature TOR values is probably the different levels of approach to the high activity steady state reported in this work. In the current work, the long steady-state reaction as well as the conditions of the reaction insure a fully activated catalyst. Note that the values of the TOR reported in this work (Table 4) are close to the maximum values reported in the literature.

To confirm the trends on the Pd surface area measurements determined by chemisorption, the Pd particle size was also measured by XRD line broadening. The results are collected in Table 3. Samples 2, 4, and 6 show reasonably good agreement between XRD and chemisorption particle size results. Samples 1 and 3 show chemisorption particle sizes 2.5–3.0-fold higher than the XRD particle size. These samples were calcined at 973 K, of which PdO is the stable phase and the sample is fully oxidized to PdO as shown by XRD. Subsequent treatment in H_2 at 373 K in the titration measurement reduces the PdO to Pd, again confirmed by XRD. This low temperature reduction is probably insufficient to anneal the sample, resulting in polycrystalline particles with an XRD crystallite size smaller than the chemisorption particle size.

TABLE 4

Comparison of Turnover Rates for the Oxidation of Methane over Supported Pd Catalysts

TOR[a] (s^{-1})	Particle size (nm)	E_a (kJ mol^{-1})	Reference
7×10^{-3}–1×10^{-1}	1.4–5.6	71–84	Yao (4)
1×10^{-4}–2×10^{-2}	1–30	110–125	Hicks *et al.* (6, 7)
3×10^{-3}	3	—	Oh *et al.* (9)
3×10^{-2}	16	—	Briot and Primet (23)
1×10^{-4}–2×10^{-2}	2–80	80–160	Baldwin and Burch (31)
2×10^{-2}–8×10^{-2}	2–110	75–90	This work

[a] Rates recalculated for a reaction temperature of 550 K in 2% CH_4/air.

Although the surface area measurements by XRD and chemisorption show reasonable agreement, they do not directly measure the number of active sites; PdO, not Pd, is the stable bulk phase under reaction conditions used in this work. It is possible that some of the interactions between PdO and the support are modified when PdO is reduced to Pd before the chemisorption and XRD measurements. The possibility that the PdO surface area is changed by reduction at 373 K during the titration measurement was tested by running the reduction and chemisorption at RT. In this case, a backsorption is needed to subtract the amount of absorbed H_2 (15). The chemisorption results, however, were very close to results on the standard reduction experiments at 373 K. Even the reduction by hydrogen at room temperature may change the PdO active surface area, although it seems improbable; a method should be devised in the future to measure the PdO surface area directly.

The data summarized in Table 3 show a variation in the TOR of 2×10^{-2} to 8×10^{-2} s^{-1}. However, these samples have been pretreated in air from temperatures of 773 to 1123 K. Treatment in air at 773 or 973 K, temperatures at which PdO is the thermodynamically stable phase, has been shown to oxidize the Pd to PdO and to spread the PdO onto the support surface as a thin surface layer, probably forming a molecular complex of PdO on the oxide surface (11, 14). The mild reduction used in the titration measurements of Pd surface area (373 K) reduces this spread PdO layer but does not cause it to sinter to the extent found after treatment in air at 1123 K. Comparison of data set number 2 (Table 3), for a sample treated at 1123 K and quenched, to data set number 1, for the sample subsequently treated at 973 K, shows an increase in measured Pd surface area of 3.2-fold. This increase is a result of spreading of PdO onto the support surface. Comparison of the per gram rate for methane oxidation on these two samples shows no change in rate. Clearly, the PdO layer spread onto the support surface is not active. A similar comparison of data sets 3 and 4 shows a Pd surface area increase of 2.6 with a rate increase of only 1.3. This comparison suggests that the PdO phase spread over the support surface is relatively inactive. The bulk PdO phase formed on the metallic Pd particles has the highest per site activity.

Comparison of the samples pretreated at 773 or 973 K, for which PdO is the stable phase, shows a TOR range of 2×10^{-2} to 5×10^{-2} s^{-1}. This 2.5-fold rate variation occurs for a particle size range of 2 to 40 nm. Similarly, comparison of the samples treated at 1123 K and quenched shows a TOR range of 4×10^{-2} to 8×10^{-2} s^{-1}. This is a rate variation of twofold for a particle size range of 60 to 120 nm. These results suggest that particle size, support, and Pd metal precursor have a minimal effect on the TOR and that the oxidation of CH_4 in excess O_2 is a structure insensitive reaction.

The two- to fourfold variation in TOR observed here for supported Pd may be due to other effects, including the support (8), residual chlorine on some of the catalysts (32), or other variations between these catalysts.

5. CONCLUSION

For the oxidation of CH_4 over supported Pd catalysts, the turnover rate does not depend on the Pd precursor, support, or Pd particle size *if* the catalysts are fully activated before the rate measurements are made. Under steady-state conditions, it is concluded that the reaction is *structure insensitive*.

The large differences in the turnover rates in the literature are attributed to the use of incompletely activated samples. The initial rate may vary somewhat for different Pd catalysts; however, an initial reaction rate could not be measured.

The oxidation of CH_4 over PdO is strongly inhibited by CO_2 and H_2O. Assuming a power rate law expression, $r = [CH_4]^a[O_2]^b[H_2O]^c[CO_2]^d$, the dependence on H_2O was -1 order over the entire range studied. Inhibition by CO_2 was more complicated, with about zero order below 0.5% CO_2 and about -2 order above 0.5% CO_2. This strong product inhibition could also account for some of the variation in reaction rates reported in the literature.

Treatment of supported Pd catalysts in air at atmospheric pressure and temperatures below about 1000 K results in the formation of the stable PdO phase, which spreads as a monolayer on the oxide support surface. This dispersed monolayer phase of PdO appears to have a low catalytic activity.

ACKNOWLEDGMENTS

We thank Dr. Stefan Justi for the XRD measurements and Mrs. Sophia Bloch for the BET and chemisorption measurements.

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