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The effect of water on the activity of supported palladium catalysts in the catalytic combustion of methane

J.C. van Giezen, F.R. van den Berg, J.L. Kleinen, A.J. van Dillen, J.W. Geus*

Department of Inorganic Chemistry, Debye Institute, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, Netherlands

Abstract

Supported palladium catalysts are very active in the combustion of methane, but still little is known about the kinetic parameters. In this paper a rate expression is presented for an alumina-supported palladium oxide catalyst in the temperature range 180–515°C. Special care was taken to ensure differential conditions during the experiments. In this way, an apparent activation energy of 151±15 kJ/mol was found. The orders in methane, oxygen and water were 1.0±0.1, 0.1±0.1 and −0.8±0.2, respectively. For carbon dioxide a zero order was observed under all conditions. Inhibition by water produced during the reaction was demonstrated to cause non-differential conditions, when a dry feed was used. The rate constant that corrects for this effect could be derived. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Palladium oxide; Methane; Combustion; Water inhibition; Kinetic parameters

1. Introduction

Conventional combustion of natural gas suffers from high emissions of CO, NO_x and unburned hydrocarbons due to the high temperatures required to achieve complete combustion, and the non-selective nature of this type of gas phase reactions. Catalytic combustion offers a good alternative since complete conversion of natural gas can be achieved at fairly low temperatures. Furthermore, the selectivity of catalytic combustion is excellent as no other products than carbon dioxide and water are formed.

Many catalysts have been investigated for their activity in the combustion of methane, the main component of natural gas, and supported palladium catalysts have been reported to show the highest activity [1–3]. However, there is a lack of reliable kinetic data on catalytic combustion of methane over supported palladium catalysts. Apparent activation energies ranging from 23 to 159 kJ/mol have been found. An important property of supported palladium catalysts is that a stabilisation period is required to achieve steady state conversion [4–6]. This phenomenon is often not recognised, which has led to inaccurate kinetic data. Ribeiro et al. [7] appreciated this problem and found an apparent activation energy of 70–90 kJ/mol.

Good agreement has been found with respect to the dependence of the reaction rate on the partial pressures of the reactants, generally about a first order in methane and about zero order in oxygen [2,8,9]. Possible inhibition by the reaction products, however, has not been given much attention. It has been reported that the catalytic combustion of methane is strongly

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*Corresponding author. Fax: +31-30-2511027.

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inhibited by water vapour, but there is no consensus on the effect of carbon dioxide [7,10,11].

The aim of this study was the acquisition of a complete set of reliable kinetic data for deep oxidation of methane over (alumina-)supported palladium catalysts in the temperature range of 563–723 K. Crucial in obtaining these kinetic parameters is the requirement to execute the measurements under differential conditions. To this end a micro flow reactor was used with diluted gas feeds at low conversions. Special attention was paid to inhibition by water vapour, formed in the combustion reaction itself, which is included in the rate expression that could be derived.

2. Experimental

2.1. Catalyst preparation and characterisation

A 7.3 wt% PdO-on-alumina catalyst was prepared by incipient wetness impregnation of an alumina support (Al 4172 P, Engelhard) with a $Pd(NH_3)_4(NO_3)_2$ solution (Johnson Matthey). Subsequently the catalyst precursor was dried overnight at 333 K and calcined in air for 3 h at 723 K.

For measurements at low temperature (563 K) the pure catalyst was used, whereas at temperatures higher than 633 K, the PdO/Al_2O_3 was diluted with varying amounts of SiO_2 (Aerosil 200, Degussa AG). To this end, weighed amounts of silica and the Pd/Al_2O_3 catalyst were ground and mixed thoroughly in a mortar and pressed into pellets (2 tons/cm^2). These were broken and sieved to obtain a fraction of 0.15–0.50 mm. The activity of Aerosil 200 for the oxidation of methane was checked, and the conversion was negligible in the temperature range studied.

2.2. Procedure and apparatus

All kinetic experiments were run down flow at atmospheric pressure in a tubular quartz reactor of 0.5 cm i.d. The catalyst was placed between two beds of inert material (alumina, Al 4196 E, Engelhard, 0.15–0.50 mm). The feed was heated efficiently to the required temperature by the alumina on top of the catalyst. The inert material down flow ruled out the possibility of any gas phase reactions taking place in the post-catalyst space. Alumina had no activity in the oxidation of methane in the temperature range studied.

The product gases were analysed with a Perkin-Elmer type 8700 gas chromatograph, packed with a Porapak Q column for separation of carbon dioxide and methane. Carbon dioxide was quantitatively hydrogenated over a zirconia-supported nickel catalyst. The resulting methane was detected with a flame ionisation detector. The oxidation of methane was observed to be 100% selective towards carbon dioxide.

2.3. Catalyst testing

Stabilisation of the catalyst was executed in a feed consisting of 1% CH_4 and 4% O_2 in helium. The total flow rate, which was passed downwards through the catalyst bed, was 100 ml/min (STP). Before each kinetic measurement the catalyst was heated at 813 K for 7 h and cooled down to 313 K. Subsequently, the temperature of the reactor was varied stepwise by 5 K up from 313 to 813 K and back downwards to 313 K. If the conversion curves coincided, it was concluded that the catalyst had attained stable performance in the range of room temperature to 813 K.

Measurements of the dependence of the reaction rate on the partial pressures were executed as follows. The reactor was brought up to a temperature at which a stable conversion of about 5% could be maintained. The feed consisted of 1% CH_4, 7% O_2 and 2% H_2O in helium. The partial pressures of CH_4, O_2, CO_2 and H_2O were varied separately. The CH_4 concentration was varied between 0% and 6%, O_2 between 2% and 7%, CO_2 between 0 and 5% and H_2O between 0.6% and 3.1%. Water vapour was added to the feed by passing a mixture of CH_4, O_2 and He through a saturator. The partial pressure of H_2O was varied by controlling the temperature of the saturator.

The apparent activation energy was determined with a feed consisting of 1% CH_4, 4% O_2 and 2% H_2O in helium. The temperature of the furnace was varied stepwise by 15 K, up from 473 to 593 K and downwards from 593 to 473 K. After each step the conversion was allowed to stabilise for 15–20 min and measured several times. The conversion curves for increasing and decreasing temperature coincided.

Table 1
Orders in reactants and products

T (K)	Order in CH_4	Order in O_2	Order in H_2O
563	1.0	0.2	−0.9
633	0.9	0.1	−0.7
693	0.9	0.1	−1.0
703	0.9	0.1	−0.8
743	1.0	0.2	−0.8
773	1.0	0.1	−0.7

3. Results

3.1. *Influence of the partial pressure of reactants and products*

The results of the order measurements for methane, oxygen and water are summarised in Table 1. For carbon dioxide a zeroth order was always observed. The nearly first order in methane (1.0±0.1), and the nearly zero order in oxygen (0.1±0.1) are in agreement with the orders reported [2,8,9]. To study the effect of the partial pressure of methane over a wider range, an order measurement was executed with feeds consisting of 2 vol% of water vapour and 10 vol% of oxygen in helium. With contents of methane ranging from 0.5 to 4.5 vol%, again linear dependence was observed and an order of 0.9 was found.

In this study much care was taken to ensure that the CH_4/O_2 ratio did not exceed 0.5 (stoichiometric mixture). Van Looy [12] demonstrated that only carbon dioxide and water were observed, even at a methane/oxygen ratio much larger than 0.5. Total oxidation was the only process as long as the oxygen was partly consumed, i.e. at low levels of methane conversion. Over the whole range of partial pressures, an order of 0.9 in methane and an order of 0.2 in oxygen was found by Van Looy, which is in good agreement with the observations presented here.

The zero order in carbon dioxide corresponds very well to the observations of Cullis et al. [10,11]. The strong inhibition by carbon dioxide for concentrations higher than 0.5 vol%, as measured by Ribeiro et al. [7], could not be reproduced. The only difference with the experiments presented here is that the measurements of Ribeiro et al. were executed with a PdO-on-Si–Al_2O_3 catalyst, whereas we used a PdO-on-alumina catalyst.

For the order in water a value of −0.8±0.2 was found. This strong inhibition by water vapour is roughly in agreement with the observations of Ribeiro et al. [7], who reported an order of −1.0. The results of Cullis et al. [10,11], however, partly conflict with these observations. For thoria- and urania-supported palladium catalysts, strong inhibition by water vapour, produced during the oxidation of methane, was observed [10]. Studying alumina-supported palladium catalysts, however, Cullis et al. concluded that only relatively large concentrations of water inhibit the oxidation of methane. Amounts of water comparable with those formed by the total oxidation of methane were not found to have any significant effect on the activity of the catalyst [11]. The results presented by Cullis et al. [11], however, demonstrate that inhibition by water vapour occurs over the whole range of water concentrations, even at very low amounts of water added (which was varied from 0 to 5.5×10^{-6} mol).

The order in water we found is valid for the concentration range of 0.6–3.2 vol%. Kinetic measurements, in order to find the apparent activation energy, are usually executed at low levels of conversion. At a conversion of 20% the total water concentration at the bottom of the catalyst bed will measure 40% of the inlet concentration of methane. A typical inlet methane concentration of 1 vol%, like we used, consequently results in an exit water concentration of 0.4 vol% at 20% conversion. This concentration is significantly lower than the water contents used in the order measurements. To study the influence of water pressures comparable to those formed in the reaction itself (at low levels of conversion), the procedure for acquiring the order in water as described in this paper is not suitable. Moreover, order measurements at very low partial pressures of water present an additional problem, since the amounts of water added are of the same order of magnitude as those produced by the total oxidation of methane.

If very small concentrations of water indeed have any appreciable effect on the reaction rate, this effect should be apparent from the dependence of the conversion of methane on residence time, if a dry feed is used and if the experiments are executed at very low levels of conversion. A linear dependence would demonstrate that water produced in the reaction itself does not have any significant influence on the rate of

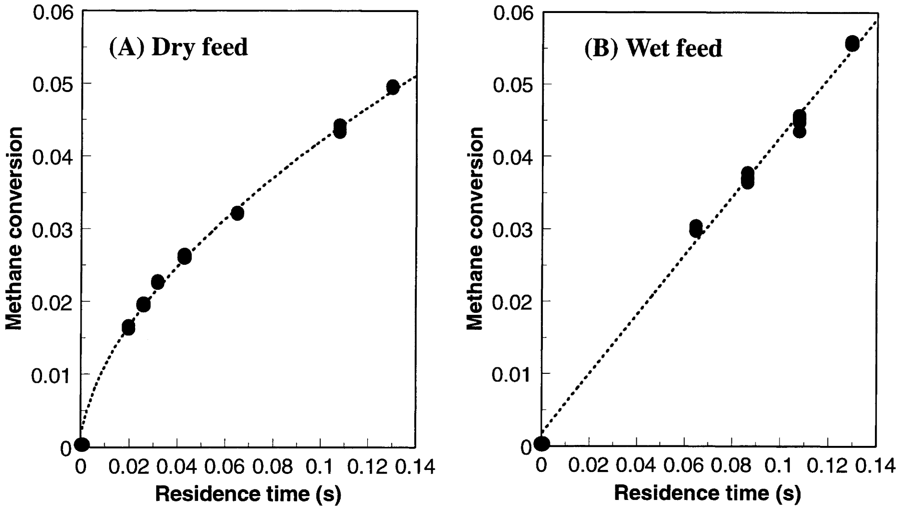

Fig. 1. Conversion-versus-residence time for a 7.3 wt% PdO/Al_2O_3 catalyst using a feed consisting of 1% CH_4 and 4% O_2 in He (A) and 1% CH_4, 4% O_2 and 2% H_2O in He (B).

reaction. Using a feed consisting of 1 vol% of methane and 4 vol% of oxygen in helium, we measured the reaction rate as a function of residence time (which was varied by varying the total flow rate for the 7.5 wt% PdO-on-alumina catalyst) at 518 K. The results are shown in Fig. 1(A).

Clearly, there is no linear relationship. The water produced in the first part of the catalyst bed will inhibit the oxidation of methane in the catalyst bed downstream. Consequently, if the amount of catalyst is doubled, a less that double conversion is expected. Similarly, increasing the residence time twice will result in a less than two-times increase in conversion.

In contradiction to the observations with a dry feed, a linear dependence must be observed when a "wet" feed is used, i.e. under conditions differential with respect to water. A feed consisting of 1 vol% of methane, 4 vol% of oxygen and 2 vol% of water in helium and a temperature of 593 K were chosen to reveal this. The result of this measurement is presented Fig. 1(B). For a "wet" feed, indeed, a linear dependence is observed.

It must thus be concluded that inhibition by water does have an appreciable effect on the activity of supported palladium catalysts, even for amounts comparable with those formed from the oxidation of methane itself. Furthermore, it must be noted that no significant effect of the temperature on the orders is observed in the range studied, neither for the reactants, nor for water.

3.2. Determination of the apparent activation energy

In order to find the apparent activation energy, we executed measurements under truly differential conditions, using a feed of 2 vol% of water, 1 vol% of methane and 4 vol% of oxygen in helium. Since there is no dependence of the reaction rate on the partial pressure of carbon dioxide, no carbon dioxide was added to the feed.

The dependence of the rate constant (k) on the temperature can be given by the Arrhenius equation, Eq. (1), and the dependence of the reaction rate on the concentrations of reactants and products by the power rate law, Eq. (2):

$$k = K\exp[-E_{\mathrm{A,app}}/RT], \tag{1}$$

$$r = k\,([\mathrm{CH_4}])^{1.0}\,([\mathrm{O_2}])^{0.1}\,([\mathrm{H_2O}])^{-0.8}. \tag{2}$$

In Eqs. (1) and (2), r represents the reaction rate (mol/l s), K the pre-exponential factor, $E_{\mathrm{A,app}}$ the apparent activation energy, R the gas constant, T the temperature in Kelvin, and $[CH_4]$, $[O_2]$ and $[H_2O]$ the concentrations of methane, oxygen and water vapour, respectively. Under differential conditions it may be assumed that the rate constant is proportional to the

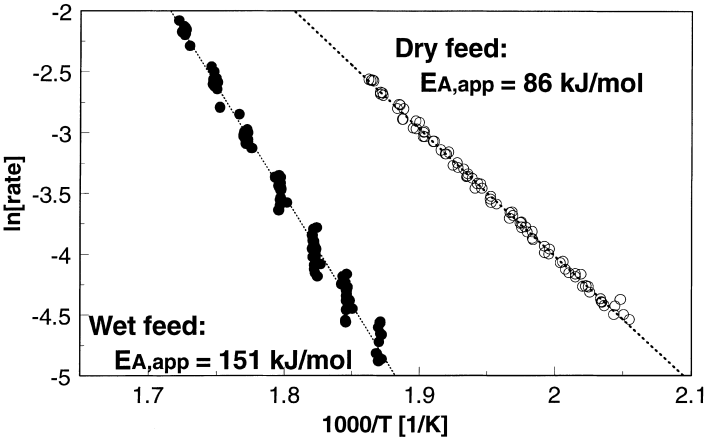

Fig. 2. The Arrhenius plots for a 7.3 wt% PdO/Al_2O_3 catalyst using a feed consisting of 1% CH_4 and 4% O_2 in He ("dry feed") and 1% CH_4, 4% O_2 and 2% H_2O in He ("wet feed").

reaction rate (r), which, in turn, at constant residence time is proportional to the conversion (x).

Since the conversion is proportional to k, the apparent activation energy can be calculated from the slope of a (pseudo) Arrhenius plot, in which ln(X) is plotted against the reciprocal temperature. The resulting Arrhenius plot for the 7.3 wt% PdO/Al_2O_3 catalyst is shown in Fig. 2. From the slope, an apparent activation energy of 151 kJ/mol was calculated. This value is significantly higher than the 70–90 kJ/mol reported in [7,13–16]. The simple explanation for this difference is that these activation energies were determined with a feed lacking an additional amount of water vapour. Consequently, the apparent activation energies have been determined under non-differential conditions.

The activity of the 7.3 wt% PdO/Al_2O_3 catalyst was also measured with a dry feed, consisting of 1 vol% of methane and 4 vol% of oxygen in helium. The resulting ln(x) versus 1000/T plot is also represented in Fig. 2. If it is assumed that the slope of this plot is equal to $[-E_{A,app}/R]$, an apparent activation energy of 86 kJ/mol is found, which is in very good agreement with 70–90 kJ mol^{-1} reported in [7,13–16]. In the next section we will provide a mathematical base to account for the difference between the activity observed with a wet and a dry feed.

4. Discussion

The activity of alumina-supported PdO catalysts is strongly inhibited by water vapour. The determination of the apparent activation energy was not executed under truly differential conditions, i.e. with dry feeds, before. Generally a first order in methane and a zeroth order in oxygen are assumed. For integral versus differential conditions, k is proportional to $-\ln(1-X)$ [16] and to the conversion, respectively. Dry feeds, however, as already mentioned, do not present differential conditions with respect to water, and the assumption that the slope of the ln(X)-versus-reciprocal temperature plot is equal to $[-E_{A,app}/R]$ is no longer valid. However, it is obvious from Fig. 1(B) that there is a linear relationship between ln(x) and 1000/T for a dry feed.

In this paper an order of −0.8±0.2 is presented, independent of the temperature in the range of 290–500°C. The dependence of the reaction rate on the partial pressure of water vapour is given by Eq. (3):

$$r = k_1\,([H_2O])^{\gamma}. \qquad (3)$$

In Eq. (3) γ is the order in water. Moreover, the reaction is assumed differential in methane and oxygen (k_1=constant) at a given temperature (T):

$$k_1 = K\,[CH_4]^{1.0}\,[O_2]^{0.1}\exp[-E_{A,app}/RT]. \qquad (4)$$

The reaction rate is related to the production rate of water vapour, as given in Eq. (5):

$$r = -d[CH_4]/dt = \tfrac{1}{2}d[H_2O]/dt. \qquad (5)$$

Eq. (6) can be derived, by combining Eqs. (3) and (5):

$$2k_1 dt = [H_2O]^{-\gamma}d[H_2O]. \qquad (6)$$

Eq. (6) can be integrated over the whole catalyst bed, so t must be integrated from $t=0$ to $t=\tau$ and $[H_2O]$ from $[H_2O]_{in}$ to $[H_2O]_{out}$. If validity of Eq. (3) is assumed for very low water vapour pressures, i.e. if γ is no function of $[H_2O]$, Eq. (7) results for a dry feed, i.e. for $[H_2O]_{in}=0$:

$$[H_2O]_{out} = [(1-\gamma)\,2k_1\,\tau]^{1/(1-\gamma)}. \tag{7}$$

Since $[H_2O]_{out}$ is related to the conversion of methane (X), Eq. (8), the $\ln(X)$ versus $1/T$ relation can now be derived.

$$x=([CH_4]_{in}-[CH_4]_{out})/[CH_4]_{in}=\tfrac{1}{2}[H_2O]_{out}/[CH_4]_{in}, \tag{8}$$

$$k_2 = -\ln(2\,[CH_4]_{in}) + [1/(1-\gamma)] \times \ln[2\,(1-\gamma)\,K\,[CH_4]^{1.0}\,[O_2]^{0.1}], \tag{9}$$

$$\ln(X) = k_2 - [1/(1-\gamma)\,(E_{A,app}/RT)] + [1/(1-\gamma)\ln(\tau)]. \tag{10}$$

Eq. (10) demonstrates that, if residence time is kept constant, i.e. $[1/(1-\gamma)\ln(\tau)]$ does not alter, and if γ is not a function of either the temperature or the water concentration, a linear relationship between $\ln(X)$ and $1/T$ will be expected for a dry feed. Now the slope of the $\ln(x)$-versus-$1/T$ plot for a dry feed is not equal to $[-E_{A,app}/R]$, but to $[-1/(1-\gamma)\,E_{A,app}/R]$. From the slopes of the $\ln(x)$-versus-$1/T$ plots of a dry and a wet feed, the order in water (γ) can be calculated. If we use the values of the slope times R of 86 and 151 kJ/mol, respectively, an order in water of -0.76 is found, in good agreement with the measured order of -0.8 ± 0.2. Also, the true apparent activation energy can be calculated from measurements with a dry feed, if the order in water vapour is known.

Similarly to the situation for varying temperature at constant residence time, the dependence of the conversion on residence time can be determined under isothermal conditions, i.e. if $[1/(n+1)\,(E_{A,app}/RT)]$ is constant. From Eq. (1) it follows that if $\ln[x]$ is plotted as a function of $\ln[\tau]$, and if this plot is linear (validity of the Power rate law), the order in water can be calculated from the slope.

In Fig. 3 $\ln[x]$ is plotted versus $\ln[\tau]$, for the same data as represented in Fig. 1(A). Obviously, a fairly straight line is obtained. Moreover, from the slope an order in water of -0.74 was calculated. This value is, again, in good agreement with the measured value of -0.8. A last remark must be made about the similarity that is observed between inhibition by water at very low and at high concentrations, respectively. Since the calculated values of -0.76 and -0.74 are in good agreement with the order measured at much higher partial pressures, it appears that inhibition (order in water) is not a function of the water concentration. This implies that the above discussion only holds true if the Power Rate Law is valid over very broad ranges of partial pressures. On the other hand, the results presented in this study give some confidence that the Power Rate Law describes the dependence on partial

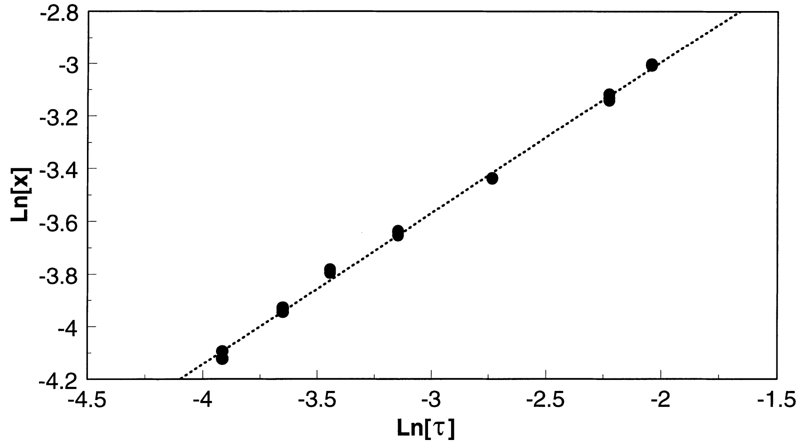

Fig. 3. Dependence of $\ln[x]$ on $\ln[\tau]$ for a feed consisting of 1% CH_4 and 4% O_2 in He.

pressures fairly well, despite the empirical nature of this equation.

5. Conclusions

Measurements of the kinetic data for the total oxidation of methane over alumina-supported palladium catalysts under truly differential conditions, i.e. with a wet feed, give an apparent activation energy of 151 kJ/mol. Furthermore, a nearly first order in methane (1.0±0.1), a nearly zeroth order in oxygen (0.1±0.1), an order of -0.8 (±0.2) in water vapour, and a zeroth order in the partial pressure of carbon dioxide are found. An empirical formula was derived with which the order in water can be calculated from either the difference in activity in dry and wet feeds, or from the dependence of the conversion on the residence time with a dry feed.

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