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Methane oxidation over PdO_x: on the mechanism for the hysteresis in activity and oxygen content

P. Salomonsson, S. Johansson and B. Kasemo [1]

Department of Applied Physics, Chalmers University of Technology,
S-412 96 Gothenburg, Sweden

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A conceptual picture is developed to explain the peculiar kinetic features of methane oxidation over supported Pd catalysts (observed by several investigators), notably the hysteresis in activity accompanying temperature cycles. Experiments were performed with supported Pd-catalysts to illustrate these features. The activity hysteresis is closely coupled with a hysteresis in oxygen content. The latter is in turn attributed to the properties of the PCT-diagram of the involved three-phase system; gas phase O_2 and the two solid phases, Pd and PdO_x. The two main ingredients in the mechanism are: (i) the so-called absorption and decomposition "plateau" pressures for the O_2–Pd–PdO_x system are different, i.e., show a hysteresis, (ii) these pressures are not independent of x, but increase with increasing oxygen content. Both features are deviations from the "ideal" three-phase system and are frequently observed for H_2–metal–metal hydride systems.

Keywords: Pd; PdO; O_2–Pd interaction; activity hysteresis; methane oxidation

1. Introduction

Supported Pd catalysts are currently receiving vivid interest. One reason is their high activity and peculiar kinetic behavior vis-à-vis methane oxidation/combustion [1–8]. The unusual kinetics include a *decrease in activity* with *increasing temperature* around 950–1100 K, and an associated *hysteresis*, as the temperature is cycled up and down, both in activity (fig. 1a) and in oxygen content (fig. 1b) [1–3,8,9].

A prerequisite to understand the activity variation with temperature and the hysteresis effects quoted above, is to understand how the oxygen content of Pd catalysts varies with the composition of the reactant mixture (O_2 pressure and O_2/CH_4 ratio) and with temperature.

PdO is frequently quoted to be the more active phase for methane oxidation, while metallic Pd appears to be much less active (see, e.g. refs. [1,6]). The O/Pd stoi-

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[1] To whom correspondence should be addressed.

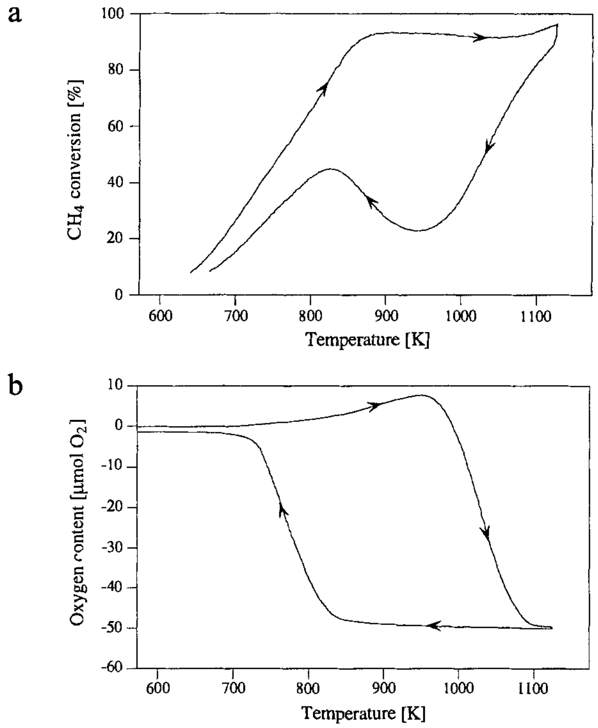

Fig. 1. (a) Hysteresis in methane conversion versus temperature for the model catalyst with low Pd load. Gas composition: 3.3% CH_4, 13.1% O_2, 83.6% Ar. $P_{tot} = 1$ atm. Temperature program: linear increase in temperature to 1123 K (rate 40 K/min), 3 min at 1123 K and then a linear decrease (rate 20 K/min). (b) Hysteresis in oxygen content for the model catalyst with high Pd load (the same catalyst as in fig. 2).

chiometry for maximum activity is not well established, motivating the use of PdO_x rather than PdO to denote the active phase. It is frequently assumed, explicitly or implicitly, that the role of oxygen is to increase the activity per site, but variations in surface area with oxygen content may also be contributing to the activity variations.

Several examples of the above-mentioned kinetics are found in the literature: Activity hysteresis during up and down temperature ramps was reported by Farrauto et al. and by McCarty [1,3]. Using thermogravimetric analysis Farrauto et al. also saw a hysteresis in oxygen content in both supported and unsupported Pd samples during temperature cycles in air. McCarty [3] and Sekizawa et al. [6] reported a decrease in activity with increasing temperature. The higher the oxygen partial pressure the higher the temperature at which the activity decline starts [6]. Sekizawa et al. attributed the activity loss with increasing temperature to the decomposition of PdO to Pd, an interpretation which was supported by in situ XRD data.

The crucial role of oxygen content, both for the activity decline at high temperature and for the activity vs. temperature hysteresis, is thus well established, but a solid mechanistic explanation is lacking, especially for the hysteresis effects. We have in this work performed some experiments with supported Pd-catalysts in order to further elucidate the behavior summarized above. We also discuss a simple fundamental mechanism that qualitatively explains the hysteresis effects: Guided by the analogy with the thoroughly investigated H_2^{gas}–metal–metal hydride three-phase systems, we attribute the behavior of the O_2^{gas}–Pd–PdO_x system to the properties of its PCT diagram (PCT = pressure, composition, temperature).

2. Experimental

In the experiments, focusing on the oxygen uptake and release kinetics, the samples consisted of dispersed Pd particles deposited on a γ-Al_2O_3 washcoat, which in turn was deposited on a cordierite monolith. One commercial catalyst (from Heraeus) and two model catalysts (from Emissionsteknik AB; manufactured by the incipient wetness impregnation technique) were used in this study. After usage the catalysts were all analysed by atom absorption spectrophotometry, in order to determine the total Pd load on each of the catalysts. The two model catalysts contained a high and a low Pd load, respectively, compared with the commercial sample, see table 1. The washcoat of the commercial sample was estimated (by TEM/EDX measurements) to contain approximately 20% CeO_2 and 1% zirconia in addition to the γ-Al_2O_3. Control runs were performed with a catalyst containing a washcoat of $Al_2O_3 + 20\%$ CeO_2, but without Pd deposit. These control runs ascertained, for example, that there was no interference from oxygen exchange with the components of the oxide support.

The experiments were performed in a flow reactor system described elsewhere [10–13]. In short it consists of a cylindrical quartz tube reactor (13.5 mm inner diameter), in which the monolith catalyst, cut to 20 mm length, is placed. The reactor is heated by an external heating coil, and the temperature is measured by a thermocouple in one of the channels of the monolith, as described earlier [14,15]. Close to the gas exit side of the catalyst, a special quartz capillary leak [12,13] is positioned, which continuously samples gas to a mass spectrometer for on-line gas composition analysis. Oxygen uptake/release was measured as a decrease/increase of the mass spectrometer signal in O_2.

Table 1
The load of Pd in the different samples used. The loads were measured by an atom-absorption spectrophotometer

Catalyst sample	Load (μmol Pd)
model catalyst with low Pd load	3
model catalyst with high Pd load	200
commercial catalyst (containing ~20% ceria and ~1% zirconia)	40

3. Results

Exploratory measurements were made on the complete oxidation of CH_4 (to CO_2 and H_2O) in oxygen excess. Fig. 1a is taken from one such run, with $O_2/CH_4 = 4$, in a carrier gas of Ar constituting 84% of the gas mixture. The gas flow was 850 ml/min (flow velocity $v = 0.1$ m/s). The catalyst was pretreated with a similar run, but in a stoichiometric mixture. The rate curve in fig. 1a demonstrates the loss of activity above 900 K; a dip in the conversion can be seen between 900 and 1100 K. The effect is more clearly seen during the decrease in temperature; when the catalyst is cooled down in the reaction mixture the activity *increases with decreasing temperature* (for similar results by earlier investigators, see refs. [1,2]).

Fig. 1b illustrates the hysteresis in the oxygen content (determined as described later), as the catalyst is cycled up and down in temperature in a dilute stream of oxygen in Ar. Comparing figs. 1a and 1b we note the strong correlation between the activity for methane conversion and the oxygen content of the catalyst [#1]. In the following we concentrate on how oxygen is released and absorbed by the catalyst as the temperature is cycled up–down.

Fig. 2 shows an experiment performed as follows: the catalyst was heated to 1123 K and then cooled down in flowing O_2 to below 673 K. This produces, as we will see soon, a catalyst with considerable oxygen content. The oxidised catalyst was then heated with a linear T-ramp of 40 K/min in flowing gas with a constant O_2 pressure of 2% O_2 (≈ 15 Torr) with Ar as carrier gas. The O_2 signal vs. temperature, measured at the gas outlet end of the monolith, is displayed in fig. 2. Any deviation above or below the 15 Torr baseline for O_2 ("zero" on the vertical axis), corresponds to oxygen desorption or absorption by the catalyst. Fig. 1b shows

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[#1] The catalyst and flow conditions of fig. 1a were chosen to emphasize the activity hysteresis. With other catalysts (higher Pd loading) and different flow rates the activity hysteresis was also seen, but the effect was usually weaker. The catalyst and flow condition of fig. 1b were different from the ones in fig. 1a, and chosen to optimize the oxygen uptake/release hysteresis.

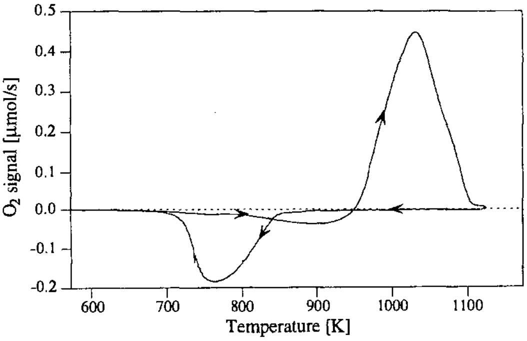

Fig. 2. Oxygen release and uptake for the model catalyst with high Pd load in a flow of 2% oxygen in Ar ($P_{tot} = 1$ atm).

the same experiment as in fig. 2, but plotted as oxygen content of the catalyst, rather than as O_2 signal. Desorption starts around 953 K, has a maximum at 1023 K and has declined considerably when 1123 K is reached. After 1 min at 1123 K the desorption rate is almost zero. From 1123 K, the catalyst was cooled down at a rate of 20 K/min. Note that no uptake is then seen in the T-range where decomposition occurred during the T-rise cycle! Uptake does not start until the temperature has been lowered to about 885 K. The maximum uptake rate occurs at 763 K. No further uptake is detected below 688 K. The likely cause for the latter is that the uptake becomes kinetically limited due to the low temperature. A small additional uptake, starting at 693 K, is seen when the temperature is raised again.

In the above experiment approximately 57.7 μmol was given off between 953 and 1123 K. 46.7 μmol was taken up on the way down in temperature. The small uptake on the way up in the temperature amounts to about 7.6 μmol. The total release divided by total uptake thus corresponds to $57.7/54.3 \approx 1.06$, where the deviation of the ratio from unity most likely is due to uncertainty in the background subtraction.

Fig. 2 thus clearly illustrates a large temperature hysteresis in the oxygen release–oxygen uptake kinetics ($\Delta T = 260$ K between the uptake and release maxima), and an associated hysteresis in oxygen content. It also shows that both uptake and decomposition occur over broad T-ranges. Two questions are of immediate interest: (i) are the hysteresis and widths of the uptake–release peaks in fig. 2 simply effects of a too fast T-ramp or are they more intrinsic properties of the PdO_x system, and (ii) how are the uptake and release peaks affected by the oxygen pressure, P_{O_2}? We address the second question first. The answer is given in fig. 3 (see also refs. [6,16,17]): An increasing O_2 pressure shifts both the uptake and release curves to higher temperature. This is the expected behavior; a higher O_2 pressure stabilises the PdO_x system through the higher oxygen potential, and thereby shifts the decomposition temperature, for a particular x-value, to higher temperature.

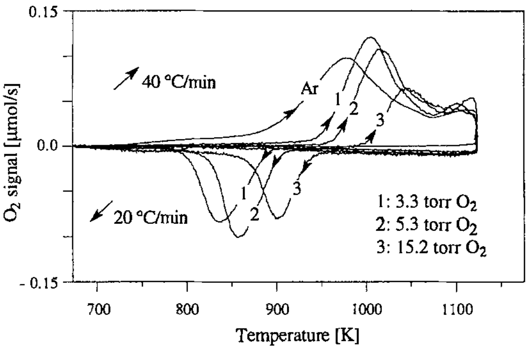

Fig. 3. Oxygen uptake and release for the commercial catalyst during T scan RT → 1123 K → RT at different oxygen pressures: pure Ar, 0.4% O_2, 0.7% O_2 and 2.0% O_2. In all cases the initial state at RT was an oxidised catalyst.

It is possible to *estimate* the heat of formation of PdO from the curves in fig. 3, by plotting the logarithm of the pressure vs. the inverse of the corresponding uptake temperature. The slope of the obtained line is the heat of formation, ΔH, according to the equation

$$\ln P = \frac{\Delta H}{RT} + \frac{\Delta S}{R} .$$

Taking for T the threshold temperatures at which absorption starts, we obtain $\Delta H = 26$ kcal/mol at temperatures around 925 K. If we use the onset temperatures of oxygen release in fig. 3 instead, the derived value for the heat of decomposition is 34 kcal/mol. These values can be compared with those from a study by Bayer et al. [16] and Bell et al. [17]. They obtained heats of formation of 25.6 and 25.8 kcal/mol at 1050 and 950 K, respectively. Their values were measured for the decomposition of PdO. Considering the very limited pressure and temperature ranges of our data, the agreement appears reasonable. (From metal hydride work it is well known that heats of formation values derived in this or similar ways, often differ for uptake and release data, respectively.)

To address the first question raised above, i.e. if the hysteresis and the large peak width are consequences of too fast temperature variation, we performed an experiment where the temperature was stepped down in small steps of 10 K per step (fig. 4). After each step the temperature was kept constant for 6 min, and the O_2 signal was continuously recorded (the average cooling rate was thus 1.7 K/min compared to 20 K/min in figs. 2 and 3). The experiment in fig. 4 clearly shows that both the width and the position of the oxygen uptake dip (figs. 2, 3) are *not* primarily consequences of slow uptake kinetics (at least not on the time scale of 10^1–10^2 min). In a similar experiment (not shown), the same procedure as above was

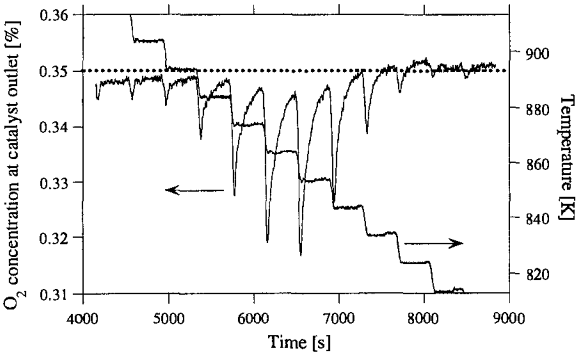

Fig. 4. Oxygen uptake during a step-wise decrease in temperature in 0.35% O_2 atmosphere for the commercial catalyst. The "stair-case" curve shows how the temperature is lowered in steps of 10 K and then held constant for 6 min. The dashed horizontal line corresponds to no uptake of oxygen, i.e. to the 0.35% O_2 of the gas feed. Note that before this experiment the catalyst was only brought up to 1003 K (not to 1123 K as in most cases). Up to 1003 K only about half of the amount of oxygen that would have been given off up to 1123 K has desorbed.

repeated, but at one point, $T = 863$ K, the constant temperature was kept for 2 h. Even after this long waiting time, oxygen uptake occurred at a subsequent step down (by 10 K) in temperature, albeit smaller in magnitude than the uptake at the same temperature in fig. 4. At the next again step down in temperature the uptake rate approached the rate shown in fig. 4.

Results similar to the ones displayed in fig. 4 for oxygen uptake were observed for the oxygen release when the temperature was raised in small T-steps. As for the oxygen uptake (during the T-down cycle), the oxygen release curve during the T-up cycle is broad and its width is not primarily determined by the speed of the T-ramp.

Summarising these observations we conclude that both the uptake/release hysteresis and the large widths of the uptake and release peaks are intrinsic properties of the O_2–PdO_x systems: Each new temperature corresponds to a different quasi-equilibrium oxygen content, the amount of which depends on whether we are on the T-up or T-down cycle. The true equilibrium content could be either the T-up or the T-down value, or some value in between. All these observations are qualitatively similar to what is observed in many metal hydride systems.

4. Discussion

Preparing for a discussion of these and related published results we note that any mechanism must explain the large hysteresis, with respect to temperature, between uptake and release of oxygen, and the broad range of temperature over which the uptake and release occur.

The proposed mechanism is actually familiar from other systems, especially from H_2–metal–metal hydride systems, but as far as we know not articulated in any detail to explain the hysteresis in the methane oxidation activity over PdO_x. The mechanism is an inherent property of a "perturbed" three-phase system ("perturbed" meaning a non-ideal system).

We regard, for the discussion, the PdO_x system as consisting of the following three phases: gaseous O_2, oxygen atoms in solution in Pd, and Pd oxide, respectively. Separate surface and interface phases are not considered for the moment [#2]. Such gas + solid solution + solid compound, three-phase systems have been investigated in great detail for metal hydride systems [18–20]. An idealised PCT-diagram is shown in fig. 5a. At sufficiently low gas phase pressure the absorbed atoms (H, O, ...) in the solid constitute a dilute solid solution (i.e. a two-phase system consisting of gas + solid solution), governed by Sievert's law [21]: $[A]_{sol} \propto \sqrt{P_{A_2}}$, for a diatomic gas A_2. At a critical concentration of dissolved atoms, X_c ($X_c \ll 1$), and a

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[#2] We make this simplification to a three-phase system, well aware that in the case of supported small particles other phases exist as well, which are likely to be important, e.g. chemisorbed oxygen and oxygen at the PdO_x–Al_2O_3 interface. We will briefly consider the possible role of these phases later in the discussion.

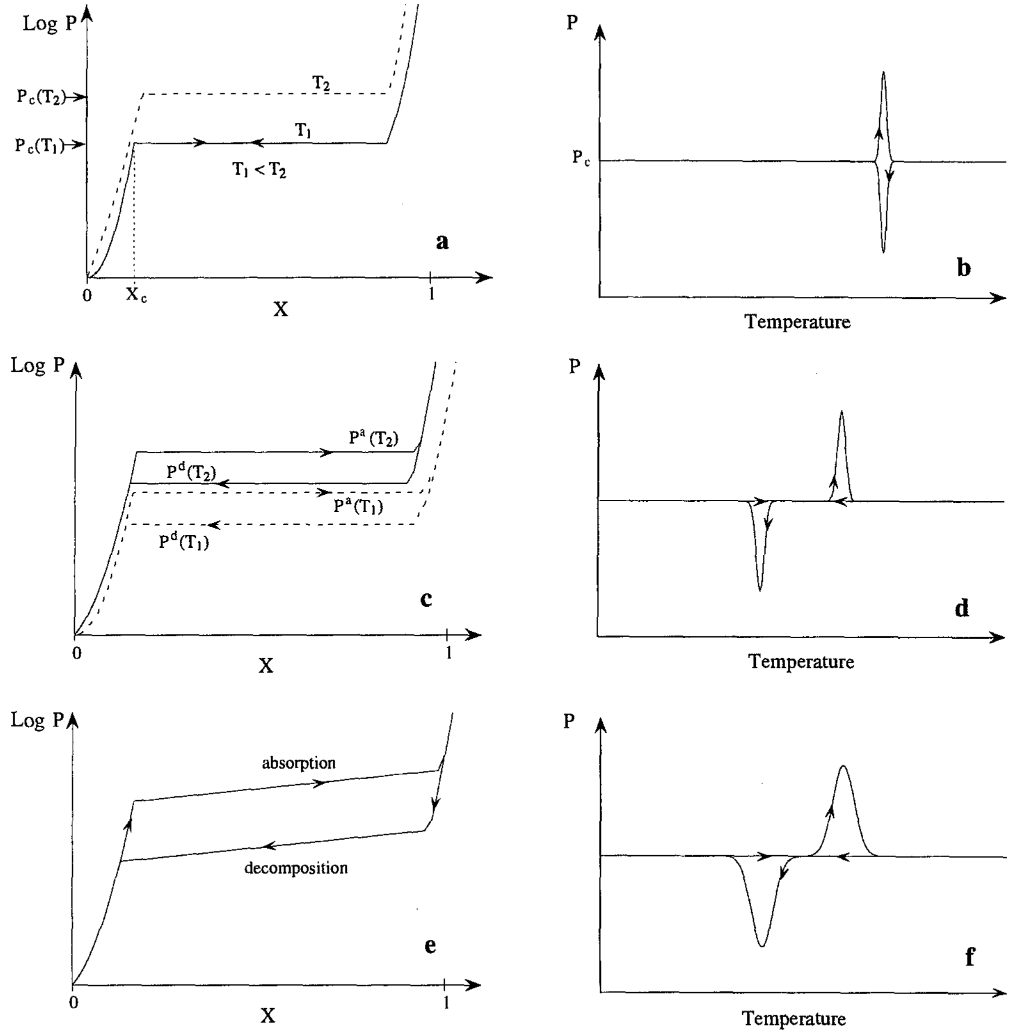

Fig. 5. (a) Schematic PCT diagram for an ideal three-phase system (e.g. gas/metal/metal-compound) at two different temperatures. (b) Schematic uptake/release during a temperature cycle for the ideal three-phase system of (a). (c) Schematic PCT diagram at two different temperatures for a three-phase system showing absorption and decomposition hysteresis. (d) Schematic uptake/release during a temperature cycle for the three-phase system of (c), exhibiting absorption and decomposition hysteresis. (e) Schematic PCT diagram for a three-phase system at constant temperature, with non-ideal decomposition and absorption pressures. (f) Schematic uptake/release during a temperature cycle for the three-phase system of (e), with non-ideal decomposition and absorption pressures.

corresponding critical pressure, P_c, a new phase nucleates and grows, ideally without further pressure increase, until ideally a saturated compound, $X \approx 1$, is formed. If we lower the pressure again, the (ideal) system decomposes reversibly without hysteresis and returns to the solid solution phase at P_c. If a higher temperature is chosen (T_2 in fig. 5a) a higher pressure is required to reach the so-called plateau pressure, i.e. $P_c(T_2) > P_c(T_1)$, and so on.

Imagine now an experiment like the one in fig. 2, where the temperature is cycled up and down at constant pressure in flowing gas, while the gas pressure is recorded. At sufficiently low temperature the system would be in equilibrium at $X \approx 1$. As the temperature is increased it eventually reaches the critical temperature, say T_1, corresponding to decomposition for the chosen pressure $P_c(T_1)$. This would produce a burst of released gas and move the system from $X \approx 1$ to $X = X_c$, and eventually to even lower X-values as the temperature is raised further. By lowering the temperature again through the critical temperature, gas species would be absorbed again at the critical temperature, rapidly converting the system from X_c to $X \approx 1$. The associated oxygen release/uptake kinetics is outlined in fig. 5b. (For the ideal system the peaks would actually be spikes of zero width. A finite width is drawn only for improved visibility.)

This idealised system contains the uptake and decomposition peaks, but lacks the temperature hysteresis and the widths of the uptake and release peaks, characteristic for the O_2–PdO_x system. However, the metal hydride systems, which are our main information source, commonly show up such hysteresis between the uptake and decomposition plateau pressures [21,22] as schematically shown in fig. 5c (often referred to as the absorption and dissociation plateau pressures, respectively).

For each temperature there is then a pressure hysteresis curve like the one in fig. 5c, which also explains the T-hysteresis. Our thought experiment with the temperature cycle would now come out as in fig. 5d. On the increasing temperature path we would see decomposition when we reach the temperature T_2 corresponding to the decomposition plateau $P^d(T_2)$ (remember that the pressure is kept constant and the temperature is varied in our experiments). On the way down in temperature nothing will happen at T_2 because the pressure is too low to reach the absorption plateau $P^a(T_2)$. We need to lower the temperature to some $T_1 < T_2$ before uptake occurs, which then corresponds to the absorption plateau pressure $P^a(T_1)$. This produces the hysteresis schematically shown in fig. 5d (again the T-widths of the peaks would ideally be zero). Since the experiment is performed at constant pressure, T_1 and T_2 are connected through $P^d(T_2) = P^a(T_1)$.

For experiments made at constant P with varying T, as in our case, this behavior is more clearly seen if we re-plot the plateau pressures $P^a(T)$ and $P^d(T)$ as log P vs. $1/T$. When there is a hysteresis, such plots produce a pair of straight, parallel lines, one line for P^a and one for P^d, as in fig. 6a. An up–down scan in temperature at constant pressure, corresponds to following the dashed horizontal line in fig. 6, from right to left (increasing T) and back again, producing the result in fig. 5d.

Applying the above general analysis to the O_2–Pd–PdO_x system, provides a simple explanation for the observed T-hysteresis in the oxygen uptake–release curves (fig. 3).

It remains to explain the large temperature-width of the decomposition and

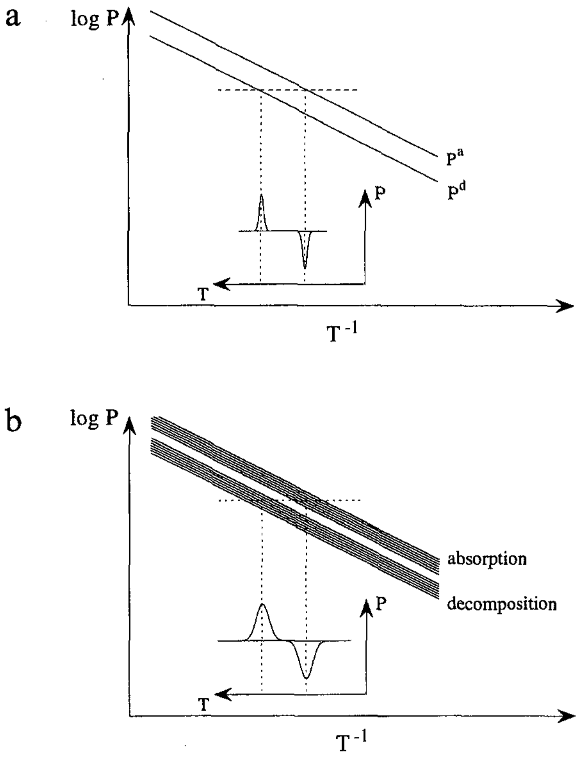

Fig. 6. (a) Decomposition and absorption pressure versus $1/T$ for a three-phase system, showing absorption and decomposition hysteresis (corresponding to fig. 5c). (b) Decomposition and absorption pressure versus $1/T$ for a non-ideal, three-phase system, with non-horizontal decomposition and absorption plateau pressures (corresponding to fig. 5e).

uptake peaks for oxygen. Again the metal hydride systems suggest an explanation: They frequently have plateau pressures that are not horizontal lines in the PCT diagrams, as in fig. 5c, but have a slope as in fig. 5e. This is especially true for cases when the metallic constituent is a thin film or consists of microscopic particles [22] but is also observed for bulk samples. For the log P vs. $1/T$ plots of fig. 6a this has the consequence that the single straight lines, representing the absorption and decomposition pressures, are replaced by two sets (or actually two continua) of parallel lines, as schematically shown in fig. 6b. The temperature cycle will now produce broad desorption and absorption peaks (fig. 5f and inset in fig. 6b), whose widths depend on the slope in the P–$1/T$ plane of the plateau pressures.

For example, with fig. 6b we can explain the result of fig. 4, where the initially decomposed (metallic) catalyst was successively lowered in temperature by 10 K steps, with 6 min at each temperature. The experiment corresponds, in fig. 6b, to moving horizontally from left to right, through the continuum of absorption pressure lines. After some time has elapsed at a new temperature a quasi-equilibrium corresponding to that temperature is established. When a new step down in temperature is taken, the equilibrium is perturbed and oxygen uptake starts again but declines as the new quasi-equilibrium is established, and so on. Analogous results were seen during uptake, corresponding to motion from right to left through the decomposition pressure lines of fig. 6b.

The above analysis thus provides an explanation for the experimentally observed hysteresis in oxygen content vs. temperature for the O_2–Pd–PdO_x system. It also explains the broad temperature range over which uptake and decomposition occurs. With this explanation for the oxygen hysteresis, we can also explain the activity hysteresis for methane oxidation in O_2/CH_4 mixtures (taking as an established fact that the activity is governed by the oxygen content of the catalyst): At low temperature the catalyst is in equilibrium in an oxidised state, PdO_x, with x near unity, which is the high activity phase. As the dissociation temperature, corresponding to the chosen O_2/CH_4 mixture, is reached [#3], the high activity catalyst is converted to the less active, metallic Pd phase and the activity decreases with increasing temperature. Due to the slope of the decomposition pressure vs. O/Pd ratio, the decomposition of PdO_x to Pd occurs successively over a fairly broad T-range. When the temperature is lowered again, the catalyst does not regain the oxygen content and the associated high activity, in the same T-range as where the oxygen was released. The activity recovery does not occur until the considerably lower temperature range corresponding to the absorption plateau pressure is reached, as observed experimentally in figs. 1–3. Again the oxygen uptake and associated reactivation occurs over a fairly broad T-range, due to the slope of the absorption pressure vs. O/Pd ratio. (In the above scenario we assumed implicitly that the role of oxygen in PdO_x is to increase the catalytic activity per site for methane activation. If instead, or as an additional effect, the role of oxygen is to increase the surface area – as indicated by some results [23–25] – analogous arguments as above can be employed to explain the activity hysteresis, but now in terms of reversible variations (with hysteresis) in surface area as the oxygen content is varied.)

A few words need to be said about the possible origin of the required absorption–dissociation hysteresis and the slope of the plateau pressure vs. O/Pd ratio. Hysteresis in the PCT diagrams is the rule rather than the exception for metal hydride systems. The hysteresis effects are not understood in detail but are connected with the stress-strain energy associated with uptake/decomposition (due to lattice expansion/contraction), resulting in generation/annihilation of dislocation networks [18–20]. The mechanism for the hysteresis is most likely of both thermodynamic and kinetic origins [19]. Although it is conceivable that the two plateau pressures are iso-energetic and purely thermodynamical states this is not very likely in view of the expected built in strain/stress in the particles and between the parti-

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[#3] Note that this dissociation temperature in $CH_4 + O_2$ is *not* the same as in pure O_2 of the same P_{O_2}. The consumption of O_2 by CH_4 oxidation counteracts the O_2 potential. Thus with CH_4 in the mixture the dissociation temperature is lowered.

cles and the support, as the oxygen content is varied. Another potential kinetic contributor to the hysteresis is a change in the wetting between the particles and the support (a different wetting for PdO_x than for Pd).

For *bulk* Pd in O_2 a horizontal dissociation plateau has been reported [26]. Hysteresis effects were not investigated, but the kinetics was reportedly very slow. A system of supported Pd particles of varying size is, however, expected to differ from the corresponding bulk system and to have a spectrum of PCT diagrams, e.g., due to particle-size dependent interfacial and surface energies, and with likely contributions also from internal strain energies due to the interaction with the support. Another way of expressing this is that small particles have a much larger relative contribution from surface and interface phases than macroscopic systems which are dominated by their bulk phases. Thus thin films and/or small particle systems are generally expected to have non-horizontal dissociation and absorption PCT diagrams – as reported for metal hydride systems [27–30] – even when the corresponding bulk system has zero or much smaller slopes.

Consequently we expect catalysts consisting of supported Pd particles of varying size to exhibit both the hysteresis and the non-horizontal decomposition–absorption plateau pressures required for the mechanism discussed above. We also expect systems with different particle size distributions and/or different supports to behave qualitatively in the same way but with quantitative differences, e.g., with respect to where the absorption and decomposition peaks appear on the T-scale, and with respect to the widths of the peaks. Experimental quantification of the PCT diagrams for supported Pd particles of controlled size is therefore an important issue to further advance our understanding of the kinetic behavior of the CH_4/O_2–Pd–PdO_x system.

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