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Rate of oxidation of CO on Pd at pressure between 10^{-1} and 10^{2} mbar

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At 445 K, and equimolar ratio of reactants, the turnover rate for CO oxidation on unsupported and supported Pd is constant within experimental error between ≈ 0.1 and 100 mbar. As first proposed in 1922 by Langmuir, the overall rate is the rate of adsorption on a surface almost saturated with CO. Thus the rate is proportional to the ratio of concentrations of O_2 and CO and is pressure independent. At quasi-saturation, the few vacant sites form an ideal dilute solution in the CO–Pd solvent. Adsorption on these sites is dominated by pressure invariant interactions with the solvent. Hence, the rate obeys Langmuir kinetics and the reaction is structure insensitive.

Keywords: Catalysis; effect of pressure; structure insensitive reactions

1. Introduction

The steady-state catalytic oxidation of CO on Pd has been investigated over a wide range of pressure. At *low pressure* ($\approx 10^{-6}$ mbar) on large Pd single crystals, Pd wire [1–3], and on Pd particles supported on large α-Al_2O_3 single crystals (model Pd/α-Al_2O_3) [4], the rate of CO_2 formation is proportional to the ratio δ of concentrations $[O_2]^a[CO]^b$ below $T \approx 500$ K with a and b, close to unity, when δ is ≈ 1. The same rate expression was reported for the oxidation of CO at *high pressure* (≈ 10–10^2 mbar) on Pd(100) at 525 K [5], on a Pd wire and Pd particles supported on γ-Al_2O_3 between 473 and 623 K [6], and on Pd particles supported on α-Al_2O_3 between 478 and 507 K [7] or SiO_2 between 348 and 448 K [8]. When δ is not close to unity, a and b differ from unity [9–11]. In this paper, we consider only the case when $\delta \approx 1$, with the pressure between 10^{-1} and 10^2 mbar. *Standard conditions* are defined as 445 K and $\delta = 1.1$.

In a previous study, Landry et al. measured values of turnover rate v_t (defined as the number of CO_2 molecules produced per surface Pd atom per second) for

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CO oxidation at 10^{-1} and 10^2 mbar, 445 K, and $\delta = 1.1$ on 5 nm Pd particles supported on Al_2O_3 [12]. They found that v_t increased by a factor of about 3 as total pressure rises from 10^{-1} to 10^2 mbar. They concluded that the increase in v_t with pressure is consistent with $a > b$, both values being close to unity. More importantly, in this pressure range, the apparent activation energy E_a increased from 77 kJ mol^{-1} at 10^{-1} mbar to 112 kJ mol^{-1} at 10^2 mbar. The latter value is very close to $E_a \approx 137$ kJ mol^{-1} reported by us [13], as obtained on a continuous polycrystalline Pd film at 2.5×10^{-6} mbar and $\delta = 1.1$. Similarly, E_a was found to be ≈ 126 kJ mol^{-1} on Pd(111) at 9.3×10^{-7} mbar and $\delta = 1.3$ [2]. But lower values of E_a were found at low pressure on model Pd/α-Al_2O_3 and explained by a support effect called reverse spillover [13]. Reverse spillover was first reported for CO oxidation on model Pd/α-Al_2O_3 at temperatures higher than 500 K [14]. In reverse spillover, reactant molecules are adsorbed on the support, diffuse on its surface, then reach the support–metal interface unless they desorb before that event. Reverse spillover was shown in ref. [13] to be important for CO above 445 K and below 500 K in the CO inhibition regime at low pressure. It causes an increase in the rate of arrival of CO molecules per surface Pd atom to Pd particles which results in an increase in CO coverage Θ_{CO} from its corresponding value for unsupported Pd under the same conditions. Thus, since $v_t \propto [O_2]/[CO]$ in that range of temperature, reverse spillover depresses v_t under the value corresponding to unsupported Pd, and also affects the temperature dependence of v_t resulting in a decrease in E_a.

In the absence of reverse spillover, $E_a \approx 137$ kJ mol^{-1} at low pressure [13]. Thus, the value of E_a at 10^{-1} mbar (77 kJ mol^{-1}) is now smaller than E_a at 10^{-6} and 10^2 mbar. The present work was initiated to re-investigate the oxidation of CO at 10^{-1} mbar on Pd/γ-Al_2O_3 in order to explain the anomalous values of v_t and E_a at 10^{-1} mbar. The new values measured in the absence of reverse spillover are reported and discussed in this paper.

2. Experimental: oxidation of CO on Pd/γ-Al_2O_3 at 10^{-1} mbar

The experimental apparatus was the same as the one used by Landry et al. in their experiments at 10^{-1} mbar [12]. Three Pd/γ-Al_2O_3 catalysts (Engelhard Industries) were used with 1.2, 4.9, and 9.1 wt% Pd. The 4.9 wt% Pd catalyst was the same as used in ref. [12] and had 21% of the metal atoms exposed at the surface, as determined by CO and O_2 chemisorption and H_2 titration of pre-adsorbed oxygen [15]. The percentage of Pd exposed for the 1.2 and 9.1 wt% Pd catalysts were measured at about 45% and 20%, respectively, by O_2 chemisorption and titration of pre-adsorbed hydrogen and H_2 titration of pre-adsorbed oxygen. The 1.2, 4.9, and 9.1 wt% Pd catalysts were diluted respectively at a 7 : 1, 13 : 1, and 27 : 1 ratio in the same Al_2O_3 (Alcoa Chemicals, T-61) calcined at 623 K for 3 h and used in ref. [12]. The alumina, which was previously ground, and the catalyst were separately sieved to the 200–400 mesh particle size range, and physically mixed. The Pd content of 1.2 and 9.1 wt% Pd/γ-Al_2O_3 and of the mixtures was checked by inductively coupled plasma after being vacuum dried at 378 K for one hour.

In each experiment, about 60 mg of 200–400 mesh diluted catalyst was placed between two plugs of acid washed and calcined (2 h at 773 K) glass wool in a U-shaped reactor. The temperature of the catalyst bed was measured with a chromel–alumel thermocouple attached to the outer wall of the reactor. The catalyst was reduced at atmospheric pressure for 2 h at 573 K in H_2 flowing at ≈ 0.17 cm^3 s^{-1}. In a first series of experiments (I) on the 4.9 wt% Pd catalyst, a mixture of 3.48% H_2 in N_2 was used as flowing H_2. In the second series of experiments (II) conducted a year later on all three catalysts, pure H_2 was flown through the reactor.

The oxidation of CO was studied at atmospheric total pressure between 360 and 385 K on all three catalysts at 380 K. The reactant mixture (Matheson) contained ≈ 100 ppm of CO and ≈ 100 ppm of O_2 in He, and was used without further purification. The standard flow rate was chosen at 0.25–0.28 cm^3 s^{-1}. After reduction, the reactant mixture was passed over the catalyst at room temperature (rt), at which no reaction was observed. Mass 28 and 32 levels were recorded with an on-line mass spectrometer (Hewlett-Packard, model #5970). Then, the temperature was increased to reaction temperature and the CO and O_2 levels were measured after 20–40 min on line. Mass 28 level was corrected for mass 44 contributions by preliminary pulsing CO_2 in the reactant mixture at rt. Average conversion of CO was calculated from CO and O_2 levels at reaction temperature and at rt. This corresponded to an accuracy in v_t within ± 16, ± 15, and $\pm 14\%$ for 1.2, 4.9, and 9.1 wt% Pd/γ-Al_2O_3, respectively. Conversion of CO ranged from ≈ 2 to $\approx 40\%$. No deactivation was noticeable. Increasing or decreasing the temperature yielded the same results. Calculation of v_t was carried out with the assumption that the rate is proportional to $[O_2]/[CO]$, as shown by others under similar conditions [5–8].

3. Results

Values of v_t for CO oxidation on 4.9 wt% Pd/γ-Al_2O_3 (I) at 2.1×10^{-1} mbar, $\delta = 1.1$, and between 360 and 385 K are presented in fig. 1 together with previous data of Landry et al. [12] obtained on the same Pd catalyst diluted 119 times between ≈ 420 and 450 K under the same pressure conditions. A least-squares fit analysis of the data between 360 and 385 K yields an apparent activation energy of 107 ± 13 kJ mol^{-1} (with 95% confidence) which is larger than the value of 77 kJ mol^{-1} above 400 K.

A Koros–Nowak test [16,17] was performed at 380 K to investigate transport effects in the reaction experiments series II below 385 K (table 1). A higher

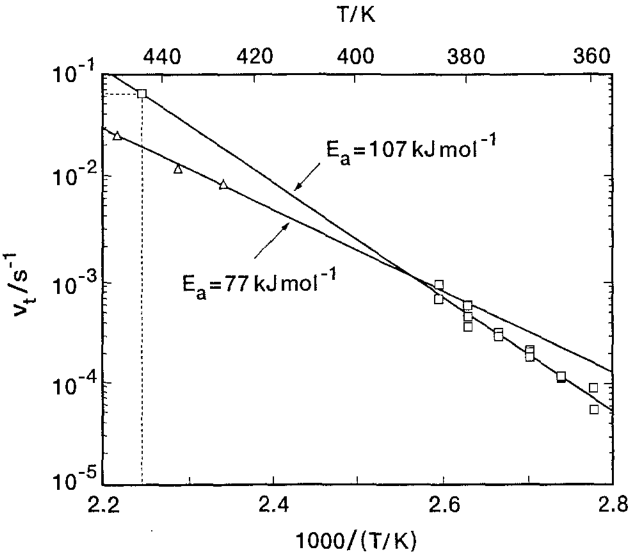

Fig. 1. Turnover rate v_t for CO oxidation at $[O_2]=1.1$, $[CO]=1.1\times10^{-1}$ mbar in He at atmospheric pressure on 4.9 wt% Pd/γ-Al_2O_3 (21% metal exposed) diluted with Al_2O_3 at a ratio 119:1 (△) [12] and 13:1 (□); solid lines represent least-squares fits of the data; the solid square corresponds to the value of v_t = 0.065 s^{-1} extrapolated at 445 K from low temperature data.

value (1.3 s^{-1}) for the sample with 4.9 wt% Pd was obtained one year earlier on the same sample (series I); the lower value (0.8 s^{-1}) was obtained together with values on the two other samples (series II). The discrepancy illustrates the difficulty of obtaining reproducible results with diluted beds at 10^{-1} mbar. Nonetheless, at 380 K, v_t remains approximately constant in series II within a factor of 1.5 as the Pd loading changes by a factor of 7.6. The larger percent of Pd exposed of the 1.2 wt% Pd catalyst has no effect on v_t because the oxidation of CO on Pd is a structure insensitive reaction [1]. Thus, the Koros–Nowak test is unambiguous and rate measurements below 385 K are free of transport effects. A value of 0.065 s^{-1} for v_t at 445 K can be extrapolated from the rate data between 360 and 385 K with E_a = 107 kJ mol^{-1} (fig. 1). The error bar for v_t at 445 K is taken to be equal to the experimental one, i.e. ±15%. The calculated v_t at 445 K is larger by a factor of 2.7 than the one measured by

Table 1
Koros–Nowak test: turnover rate v_t of the oxidation of CO on Pd/γ-Al_2O_3 catalysts at 380 K, $[O_2]=1.1$, $[CO]=1.1\times10^{-1}$ mbar in He; total pressure is atmospheric pressure (series II of experiments)

Pd (wt%)	% Pd exposed	v_t (10^{-3} s^{-1})
1.2	45	1.1 (±16%)
4.9	21	0.8 (±15%)
9.1	20	1.2 (±14%)

Table 2
Effect of total pressure on the turnover rate v_t and apparent activation energy E_a for the oxidation of CO on Pd at 445 K and $[O_2]/[CO] = 1.1$

Sample	Pressure (mbar)	v_t (s^{-1})	E_a (kJ mol^{-1})	Ref.
Pd/γ-Al_2O_3	2.1×10^{-1}	0.065 (±15%) [a]	107	this work
Pd/γ-Al_2O_3	1.1×10^{2}	0.074 (±16%)	112	[12]
Pd(100)	2.0×10^{0}	0.077 [a]	113	[11]
Pd(110)	3.2×10^{1}	0.070 [a]	109	[5]

[a] Value interpolated or extrapolated (see text).

Landry et al. We believe that low values of v_t and E_a at high T are caused by reverse spillover of CO from the support to the Pd particles in analogy with low pressure results on model Pd/α-Al_2O_3 [13], as explained in the introduction. A more detailed investigation, which will be published separately, will address this problem and, in particular, show that pore diffusion effects can be ruled out [18].

The effect of total pressure on v_t at the standard conditions ($T = 445$ K, $\delta = 1.1$) is presented in table 2. The turnover rate and E_a at 1.1×10^2 mbar were measured at 0.074 s^{-1} and 112 kJ mol^{-1} on the 4.9 wt% Pd catalyst (undiluted) used in this work [12]. Results for Pd(110) are obtained from data by Berlowitz et al. [5]. The authors measured v_t and E_a for CO oxidation on Pd(110) at 32 mbar, $\delta = 0.5$, and between 450 and 625 K, and found that v_t is proportional to $[O_2]/[CO]$ and $E_a = 109$ kJ mol^{-1} below 460 K. Their value of v_t at ≈ 452 K, i.e. ≈ 0.05 s^{-1}, was corrected to 445 K using the reported value of E_a and then multiplied by 1.1/0.5 to adjust δ from 0.5 to 1.1, at a constant total pressure of 32 mbar. The calculated value for v_t at our standard conditions is equal to ≈ 0.070 s^{-1}. A similar procedure was used to correct the value of $v_t = 0.070$ s^{-1} for CO oxidation on Pd(100) at 457 K, 2 mbar and $\delta = 0.5$ reported by Logan and Paffett [11]. Under these pressure conditions, $E_a = 113$ kJ mol^{-1} between 457 and 546 K and $v_t \propto [O_2]$ at 475 K; unfortunately the order with respect to CO, b, was not measured. Since E_a is close to the value for Pd(110) [5], it was assumed that $b = 1$, and v_t at our standard conditions and 2 mbar was calculated to be 0.077 s^{-1}. It must be noted that our data on a supported Pd catalyst are in excellent agreement with those reported by two groups of investigators working with two different faces of single crystal Pd (table 2).

In a recent molecular beam study of CO oxidation on a Pd foil, Coulston and Haller measured CO conversion versus temperature at an equivalent pressure of 10^{-3} mbar and $\delta = 1.0$ [19]. Although the reported value of $E_a = 118$ kJ mol^{-1} in the CO inhibition regime agrees well with other results, the turnover rate at 445 K is much larger than v_t at HP but, as suggested by the authors, the gas temperature of the reactants was colder than, and therefore not in equilibrium with, the surface temperature. For this reason we have not entered these results in table 2.

4. Discussion

The classical rate expression $v_t \propto [O_2][CO]$, which was first obtained by Langmuir for CO oxidation on a Pt wire at 1.3×10^{-3} mbar [20], was observed in the pressure range shown in table 2. It can be derived simply from three assumptions: first, the rate determining step is the one-way chemisorption of O_2 [21]; second, the rate is equal to the rate of adsorption of O_2 on a metallic surface saturated with adsorbed CO; and third, the surface is uniform in the Langmuir sense, i.e. all sites are identical and there are no interactions between adsorbed species [22].

With these assumptions, the rate equation is

$$v_t = k[O_2]/K[CO], \tag{1}$$

where k is the rate constant of the chemisorption of O_2 at concentration $[O_2]$ and K is the equilibrium constant for the chemisorption of CO at concentration [CO].

Unfortunately, information on k and K is lacking except at low surface coverage. While adsorption of O_2 is not activated on bare Pd, Pt, and Rh, it becomes completely inhibited below 300 K on a Pd(111) surface precovered with CO at a fractional coverage Θ_{CO} larger than 0.33 [23]. Many studies have been reported on the variation of $-\Delta H$, the integral or differential enthalpy of adsorption of CO on palladium single crystals or polycrystalline films [24–32]. The value of $-\Delta H$ generally goes down as Θ_{CO} increases. The question is what are the values of k and K at saturation coverage, i.e. $\Theta_{CO} \approx 1$? There is no answer at the moment to that question. Yet, under our standard conditions, everything happens as if Θ_{CO} were near unity between 10^{-1} and 10^2 mbar.

4.1. SATURATION COVERAGE OF CO AT HIGH PRESSURE

We define Θ_{CO} as the number of adsorbed CO molecules per surface Pd atom. The value of Θ_{CO} has not been measured quantitatively during steady-state CO oxidation on Pd at the pressures of interest in this work, but indirect experimental evidences suggest that it is close to unity. It is well established that $\Theta_{CO} \approx 1$ for the chemisorption of CO at rt and pressures as discussed in this work, since CO chemisorption is routinely used with supported Pd catalysts to measure the percent metal exposed: it is clear that one CO molecule titrates one surface Pd atom [15,33,34]. The presence of O_2 in the gas phase and temperatures above rt may alter the equilibrium value of Θ_{CO} because of reaction between adsorbed CO and O atoms. Yet, Baddour et al. observed no change in the infrared spectrum of CO adsorbed on Pd particles supported on SiO_2 and exposed at rt to CO at 0.05 mbar when O_2 was added at 0.28 mbar to the gas [35]. The infrared spectrum at saturation CO coverage contained two intense absorption bands at 2095 and 1990 cm^{-1}, and no CO_2 was detected under these conditions. However at 416 K, in addition to detection of CO_2, an overall decrease by about 10% in infrared transmission over the whole spectrum was observed which indicated a drop in Θ_{CO}, when the total pressure was decreased from 0.5 to 0.4 mbar at constant $\delta \approx 0.3$. The intensity of infrared bands for CO at 9.5 mbar and 416 K was only about 5% lower than at rt and 0.05 mbar of CO. Yet, the rate of CO oxidation was approximately the same at both pressures. Thus, although Θ_{CO} decreases slightly with decreasing total pressure at constant δ, the classical rate expression still applies and the assumption of a Pd surface saturated with adsorbed CO during reaction seems to remain valid. Kember and Sheppard investigated the infrared absorption spectrum of CO adsorbed on a Pd supported on SiO_2 catalyst during steady-state CO oxidation at temperatures between 291 and 473 K, $0.1 \leqslant \delta \leqslant 10$, and total pressures between 5 and 80 mbar [36]. The spectra of adsorbed CO were similar to the ones obtained by Baddour et al. The intensity of the adsorption bands decreased with increasing δ and T and decreasing pressure. Similar results have been obtained recently by Choi and Vannice for steady-state CO oxidation on Pd supported on δ-Al_2O_3 catalysts [10]. Thus it appears that, at pressures and temperatures used in this work, the surface of Pd is almost saturated with CO. But why does the CO covered Pd surface behave as a uniform surface during steady-state CO oxidation under the conditions of this work?

4.2. UNIFORMITY OF THE METAL SURFACE NEAR SATURATION WITH CO

Adsorption of O_2 and CO occurs at vacant sites in the CO overlayer. It has been argued that, when the density of adsorbed CO is large, the adsorptive properties of the vacant sites for dioxygen are dominated by repulsive interactions with the surrounding CO molecules [37]. The magnitude of these intermolecular interactions will change only slightly with Θ_{CO} in the vicinity of complete coverage, because of the small number of vacant sites present in the CO overlayer. In that case, $-\Delta H_{CO}$, which has been shown to decrease with increasing Θ_{CO}, should not change with Θ_{CO} at sufficiently high values of Θ_{CO}. The few vacant sites behave ideally like a very dilute solute in the two-dimensional CO–Pd solvent. This explanation of the uniform behavior of saturated surfaces also explains the structure insensitivity of CO oxidation on Pd in the CO inhibition regime. Indeed, the properties of the vacant sites are dominated by interactions between surrounding CO molecules and are insensitive to the underlying metal structure. Moreover, the Pd surface structure may also be reconstructed upon adsorption of CO, reinforcing the structure insensitivity of the reaction [38]. Indeed, Gaussmann and Kruse have shown with field ion microscopy that the surface of a Pd tip reconstructs when exposed to CO [39]. The surface of the Pd tip, which consisted of (111), (100), (110), (210), and (311) planes, was saturated with adsorbed CO at 300 K and 1 mbar of CO; reconstruction of Pd planes with high Miller indices into facets occurred upon CO adsorption and the terraces of the facets had the (111) and (100) orientation. Hicks et al. suggested that similar structural changes on the surface of Pd particles supported on alumina are responsible for the changes in the infrared spectrum of adsorbed CO, when the particles are exposed to CO gas at ≈ 10 mbar and rt [34]. Both surface reconstruction and intermolecular interactions result in a uniform catalytic surface under reaction conditions, which is consistent with the fact that the kinetics of CO oxidation can be described adequately by Langmuir kinetics, as shown in eq. (1). This in turn accounts for the main result of this work (table 2): v_t is constant over three orders of magnitude of pressure.

5. Conclusion

In this paper, we have shown that, at our standard conditions, the turnover rate of oxidation of CO on supported Pd is the same within experimental error at $\approx 10^{-1}$ and 10^{2} mbar. It is also the same at ≈ 1 and ≈ 10 mbar on two low index faces of large single crystals of Pd in two independent investigations.

To rationalize these observations, we have discussed five related concepts: *reverse spillover, saturation* of the surface *with* CO, *surface uniformity, structure sensitivity*, and *Langmuir kinetics*.

Reverse spillover of CO brings additional CO from the support to the Pd clusters. In the regime of inhibition by CO of the rate of CO oxidation, this effect depresses the rate, provided that the surface of Pd is not already saturated with CO adsorbed directly from the gas phase. This proviso makes it easy to understand why reverse spillover of CO depresses the rate on supported Pd at 10^{-1} mbar but not at a pressure one thousand times higher.

But what is *saturation*? The answer is through an operational definition. There is saturation in CO on Pd, for the CO oxidation on Pd at standard conditions if the turnover rate is not supposed to change with pressure. In a forthcoming paper, we will analyze the situation at 10^{-6} mbar [40]. We will conclude that at low pressure (10^{-6} mbar), the meaning of saturation is different from what it is at high pressure. At pressures higher than 10^{-1} mbar, saturation corresponds to $\Theta_{\mathrm{CO}} \approx 1$. What is meant by saturation is that the surface coverage by CO is very insensitive to changes of pressure of CO under reaction conditions.

If this condition is satisfied, the surface behaves like a *uniform surface*, i.e. all vacant sites appear equivalent thermodynamically and kinetically.

But if the surface appears uniform, the reaction should be *structure insensitive* and its kinetics should be described by *Langmuir kinetics*. These conditions are clearly satisfied for CO oxidation on Pd at our standard conditions. In particular structure insensitivity is beautifully demonstrated at high pressure by the data of table 2 showing essentially identical turnover rate on Pd(100) and Pd(110). The structure insensitivity for CO oxidation at $\approx 10^{-6}$ mbar on Pd single crystals and a polycrystalline wire was demonstrated by the early work of Ertl et al. [1].

In summary, this paper contributes one answer to the old question: why Langmuir kinetics is so often successful in modeling rate data on catalytic metal surfaces in the face of so much evidence to the contrary from surface science [41].

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