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CO Oxidation on Pt/α-Al_2O_3(0001): Evidence for Structure Sensitivity[1]

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The oxidation of CO by O_2 has been studied over model catalysts prepared by vapor deposition of Pt onto an α-Al_2O_3(0001) crystal. Reaction rates were measured for two particle sizes, 14 and 1.7 nm, in order to determine whether this reaction is structure sensitive and how the rates were affected by changes in the desorption kinetics of CO on small and large particles which had been observed previously (E. I. Altman and R. J. Gorte, *J. Catal.* **110**, 191 (1988)). For 10 Torr each of CO and O_2, between 560 and 680 K, the turnover frequencies on the 14-nm particles were much higher than on the 1.7-nm particles, and the activation energy, 30 ± 3 kcal/mol, was much lower than that found on the smaller particles, 41 ± 4 kcal/mol. A simple model of the reaction demonstrates that changes in the desorption kinetics of CO with particle size can explain the observed structure sensitivity found in the reaction rates. The results indicate that adsorption studies on model catalysts can be used to understand the properties of real catalysts.

INTRODUCTION

CO oxidation by O_2 over Pt has been studied extensively due its industrial importance and relative simplicity compared to other heterogeneous reactions. (For reviews of CO oxidation, see Refs. (*1–3*).) However, the question about whether or not this reaction is structure sensitive has not been answered definitively. Although structure sensitivity has been observed under vacuum conditions (*30, 31*) and there have been some reports that indicate the turnover frequency depends on metal particle size at higher pressures (*4*), most work in this area appears to indicate that the reaction is insensitive to catalyst structure at higher pressures where the reaction is inverse first-order in CO (*1, 5–8*). This structure insensitivity is surprising given that desorption rates for CO vary strongly with crystallographic surface (*9*) and particle size (*10–12*). In particular for the regime in which the rate is proportional to P_{CO}^{-1}, one would expect that desorption kinetics should strongly affect the reaction rates.

Catalysts prepared by vapor deposition of Pt onto an α-Al_2O_3(0001) single crystal provide an ideal experimental model for testing for structure sensitivity. In recent studies, it has been shown that Pt interacts weakly with the sapphire surface, forming three-dimensional particles following deposition at room temperature (*11, 12*). The size of the particles can be varied over a wide range by changing the amount of Pt which had been deposited, and the distribution of particle sizes, determined by transmission electron microscopy (TEM), is reasonably narrow on this substrate (*13*). Temperature programmed desorption curves for CO from these model catalysts demonstrated that the desorption kinetics change significantly as a function of particle size. For very small particles (~2 nm), the desorption peak temperature for a saturation exposure of CO is ~510 K, while the corresponding peak temperature for very large particles is ~400 K. By comparison to results from single crystals, these changes in the desorption kinetics have been assigned to crystallographic effects on the small particles.

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In this paper, we will describe our studies of CO oxidation on Pt/α-Al_2O_3(0001), model catalysts. The results indicate that the reaction is indeed structure sensitive in the regime where the rate is inverse first-order in CO. For smaller particles, the activation energy for CO oxidation is found to be considerably higher and the reaction rates lower than that found on larger particles. These observations can be explained easily using a simple model for the reaction with desorption rates for CO obtained under UHV conditions. The reasons for the apparent structure insensitivity of CO oxidation in previous studies can also be explained.

EXPERIMENTAL

The reaction studies were carried out in a batch reactor which is identical to that used in previous rate measurements, with only slight modifications (*14*, *15*). The system consisted of a high-pressure cell, isolated from a UHV chamber by an all-metal valve. The sample was attached to a magnetically manipulated, linear-motion feedthrough which could transfer the sample from the high-pressure cell where rate measurements were carried out to the vacuum chamber where the sample could be cleaned by ion bombardment. A known metal coverage could be deposited onto the 7 × 7 × 0.5 mm, α-Al_2O_3(0001) single crystal by moving the sample into a metal beam whose flux was determined from a film-thickness monitor, as described elsewhere (*13*).

The crystal was heated by placing it on a Ta foil, which in turn could be heated resistively. All of the heating leads in the chamber were gold plated in order to minimize the reactivity of the sample holder. A chromel–alumel thermocouple, attached directly to the back side of the oxide crystal using a ceramic adhesive, was used to measure the temperature. With this configuration, the sample could be heated to ~700 K in the reaction mixtures, and the temperature of the oxide crystal appeared to be uniform. Reaction on the clean oxide crystal, without the addition of Pt, showed no measureable rates under any conditions used in our study.

The CO used for this study was research purity (99.99%) and was further purified by passing it through an activated carbon trap and then through a liquid-nitrogen trap. As in previous studies, we found that this procedure allowed a Pt surface to be exposed to 50 Torr of CO without being contaminated by carbon (other than one monolayer of molecular CO) or other impurities. The oxygen was of 99.9% purity (<0.5 ppm total hydrocarbons) and was used without further purification. A capacitance manometer was used to measure the pressure in the reactor, and the progress of the reaction was monitored by expanding samples from the reactor into the evacuated gas-sampling loop of a gas chromatograph. The conversion of CO was typically less than 1% so that the rates could be measured assuming differential conversions. A thermal-conductivity detector was used for some of the measurements; however, it was necessary to use a flame-ionization detector, with a methanator for reacting the CO and CO_2, for most of the measurements.

Two metal coverages were used in our study, 5×10^{15} Pt/cm^2 and 0.25×10^{15} Pt/cm^2. For these coverages, the average particle sizes, determined from the dispersion measured by CO adsorption (*11*–*13*), were ~14 nm and 1.7 nm, respectively. TEM studies had previously demonstrated the accuracy of the particle size estimates from dispersion measurements (*13*). All rates reported in this paper were normalized to the metal surface area determined from CO adsorption, assuming a constant site density of 1×10^{15}/cm^2. We did not observe any evidence for deactivation of the catalyst under the conditions of our experiments, and we intentionally avoided conditions which could lead to rate oscillations (*16*, *31*).

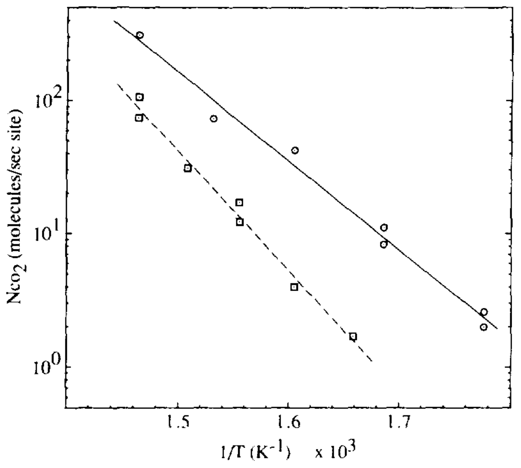

FIG. 1. Specific rates for CO oxidation on Pt for 1.7-nm (□) and 14-nm (○) particles as function of temperature for 10 Torr each of CO and O_2. The dotted and solid lines through the points are plots of Eq. (4), using the parameters in Table 1.

RESULTS AND DISCUSSION

The turnover frequencies for 1.7- and 14-nm particle sizes are shown as a function of temperature in Fig. 1 for 10 Torr each of CO and O_2. The rates on the 14-nm particles are essentially identical to those obtained previously on a Pt(100) crystal (*5*) and on Pt/SiO_2 catalysts (*17*) when the reactant pressures are extrapolated to the same values using Equation (4). The activation energy on the 14-nm particles, 30 ± 3 kcal/mol, is also close to the value reported for Pt(100), 32.9 kcal/mol. However, the rates on the 1.7-nm particles are significantly lower and the activation energy, 41 ± 4 kcal/mol, is considerably higher than that found on the larger particles.

Rates were also measured as a function of the partial pressures on the larger particles to determine the rate expression, as shown in Figs. 2a and 2b. The reaction orders for CO and O_2 at 623 K and 10 Torr each are −0.6 ± 0.3 and +1.3 ± 0.3, respectively, close to the values of −0.9 and +1.0 which have been reported previously for the pressure and temperature regime used in this study (*5*, *17*).

It is informative to compare the rates we have measured to models which have been developed for this reaction. CO oxidation over Pt has been studied by a number of groups, and the rates of the elementary steps are reasonably well known (*1*, *3*, *7*, *20*, *32*, *33*). A simple model for the overall reaction is given below:

$$\mathrm{CO} + * \underset{k_{\mathrm{CO,des}}}{\overset{k_{\mathrm{CO,ads}}}{\rightleftarrows}} \mathrm{CO}*$$

$$\mathrm{O}_2 + 2* \xrightarrow{k_{\mathrm{O_2,ads}}} 2\mathrm{O}*$$

$$\mathrm{CO}* + \mathrm{O}* \xrightarrow{k_{\mathrm{CO_2}}} \mathrm{CO}_2 + 2*.$$

The adsorption of O_2 is assumed to be irreversible at the temperatures used for this reaction, and CO_2 is assumed to be very weakly bound to the surface. The rates for adsorption of CO and O_2 can be expressed in terms of the initial sticking coefficients (S_i^0), Avagadro's number (L), the area/site (σ), and the vacant site concentration (θ_V). Following the lead of others in assuming that the adsorption rates for CO and O_2 both increase linearly with the vacant site concentration (*1*, *5*, *18*, *19*, *34*), we obtain the following rate expressions:

$$\begin{aligned} r_{\mathrm{CO,ads}} &= k_{\mathrm{CO,ads}} P_{\mathrm{CO}} \theta_{\mathrm{V}} \\ &= \frac{L S_{\mathrm{CO}}^0 \sigma}{\sqrt{2\pi M W_{\mathrm{CO}} R T}} P_{\mathrm{CO}} \theta_{\mathrm{V}} \end{aligned} \tag{1}$$

$$\begin{aligned} r_{\mathrm{O_2,ads}} &= k_{\mathrm{O_2,ads}} P_{\mathrm{O_2}} \theta_{\mathrm{V}} \\ &= \frac{L S_{\mathrm{O_2}}^0 \sigma}{\sqrt{2\pi M W_{\mathrm{O_2}} R T}} P_{\mathrm{O_2}} \theta_{\mathrm{V}} \end{aligned} \tag{2}$$

$$\begin{aligned} r_{\mathrm{CO,des}} &= k_{\mathrm{CO,des}} \theta_{\mathrm{CO}} \\ &= \nu_{\mathrm{CO,des}} \exp(-E_{\mathrm{CO,des}}/RT) \theta_{\mathrm{CO}}. \end{aligned} \tag{3}$$

The first-order dependence for the O_2 adsorption rate with site vacancies has been observed for Pt(111) and appears to indicate that the rate-controlling step in adsorption involves molecular oxygen which then dissociates later in a more rapid step (*18*, *19*). The desorption rate for CO is assumed to obey simple, first-order kinetics.

In a similar manner, one can express the

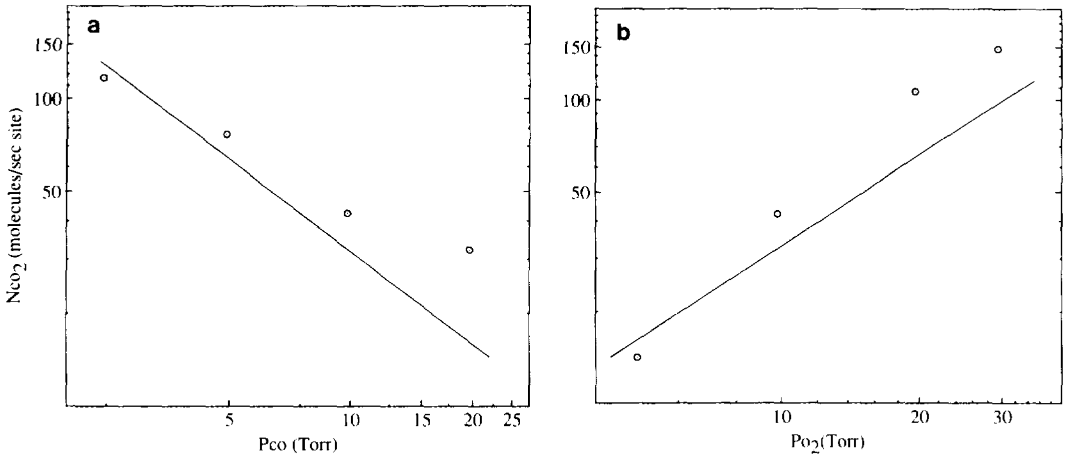

FIG. 2. Plots of CO oxidation rates as a function of (a) P_{CO} and (b) P_{O_2} for reaction at 620 K and 10 Torr of remaining reactant. The solid lines represent the predicted rates using Eq. (4) with the parameters from Table 1.

surface reaction between adsorbed oxygen and CO and solve the equations numerically to obtain the steady-state reaction rate. However, under typical reaction conditions, including those used in our study, the coverage of oxygen is much lower than the coverage of CO, primarily due to the lower sticking coefficient for O_2 compared to CO (*20*). Using this assumption, along with the fact that the adsorption rate constant for CO is much higher than the rate constant for the surface reaction between adsorbed CO and oxygen at reaction pressures, the rate expression for CO_2 production at steady state can be written in closed form with the following expression:

$$r_{CO_2} \cong \frac{2k_{O_2,\mathrm{ads}}k_{CO,\mathrm{des}}P_{O_2}}{k_{CO,\mathrm{ads}}P_{CO}}. \qquad (4)$$

This expression has been derived previously and gives the correct reaction orders for CO and O_2 (*1*, *18*). Moreover, Eq. (4) indicates that the rate of CO_2 production will depend on only four variables from the elementary reaction steps, S^0_{CO}, $S^0_{O_2}$, $\nu_{CO,\mathrm{des}}$, and $E_{CO,\mathrm{des}}$. From adsorption measurements for CO on small particles of Pt, S^0_{CO} does not appear to change with particle size and remains close to unity (*10–13*). The sticking coefficient for O_2 does change with the crystallographic orientation of Pt surfaces but appears to range between 0.001 and 0.1 (*21–23*). Both sticking coefficients are only weakly dependent on temperature, so that the activation energy of the reaction is equal to $E_{CO,\mathrm{des}}$. If one uses typical values for the sticking coefficients of CO and O_2, 0.5 and 0.01, respectively, $\nu_{CO,\mathrm{des}}$ can be calculated from the absolute values of the rates. Any errors in the assumptions for the sticking coefficients will obviously be reflected in the preexponential factor but are unlikely to change this value by more than a factor of 10. The desorption rate constants obtained from fitting the reaction rates with the above assumptions are given in Table 1.

It is interesting to examine the calculated desorption rate constants for large and small particles more closely. For the 14-nm particles, the activation energy for desorption is close to that reported for single crystals, 30 kcal/mol. The calculated preexponential, 4 × 10^{13}/s, is also between the values of 8 × 10^{12} and 6 × 10^{14}/s reported for CO from Pt(100) and Pt(110), respectively (*23*, *24*). For the 1.7-nm particles,

TABLE I

Adsorption and Desorption Rate Constants Used to Calculate the Rates for CO Oxidation from the Data in Fig. 1 and Eq. (4)

	14-nm Particles	1.7-nm Particles
S_{O_2}	0.01	0.01
S_{CO}	0.5	0.5
$E_{CO,des}$	30 kcal/mol	41 kcal/mol
$\nu_{CO,des}$	4×10^{13}/s	3×10^{16}/s
T_p[a]	470 K	530 K

[a] The peak temperature for CO desorption calculated assuming a first-order process with a constant heating rate of 7 K/sec

both the activation energy, 41 kcal/mol, and the preexponential, 3×10^{16}/s, are considerably higher. However, preexponential factors of 10^{16}/s and even higher have been observed frequently for CO desorption from group VIII metals (*25*) and can be explained easily from simple, transition-state arguments (*26*, *27*). Of additional interest are the peak temperatures that would be expected from these rate constants in a TPD experiment using a constant heating rate of 7 K/s to match that of a previous study (*11*, *12*). The values of 470 K for the larger particles and 530 K for the smaller particles are slightly higher than that obtained experimentally, as shown in Fig. 3, but are in very good agreement when one considers that the desorption features are broad for CO TPD from small particles and the extrapolation from reaction rates to desorption measurements requires a change in pressure by a factor of $\sim 10^{11}$.

These observations reinforce the picture that CO oxidation on Pt is controlled largely by CO desorption rates. Changes in the desorption rate as a function of particle size have previously been shown to be due to morphological effects rather than chemical state effects, indicating that the oxidation reaction is structure sensitive (*10–12*). This brings up a question regarding why structure sensitivity was not observed in some previous studies, given that desorption rates for CO on Pt are strongly dependent on the crystal plane and particle size, particularly at low coverages of CO. We believe that the answer lies in the fact that most Pt single crystals and all but the smallest Pt particles exhibit low-temperature features near 400 K in TPD measurements of CO. These low-temperature features occur only at high coverages of CO and are probably the result of repulsive interactions between neighboring CO molecules. Under the normal conditions for CO oxidation, the surface is essentially saturated with CO and it is the desorption rate at high coverage which is important for opening up the surface for O_2 adsorption. For very small Pt particles, the radius of curvature of the particles may effectively separate the adsorption sites and reduce the interactions between the CO molecules. In any case, the small particles do not exhibit substantially higher desorption rates at high CO coverages and, therefore, show lower rates for CO oxidation.

One should keep in mind that most rate processes on surfaces cannot be described

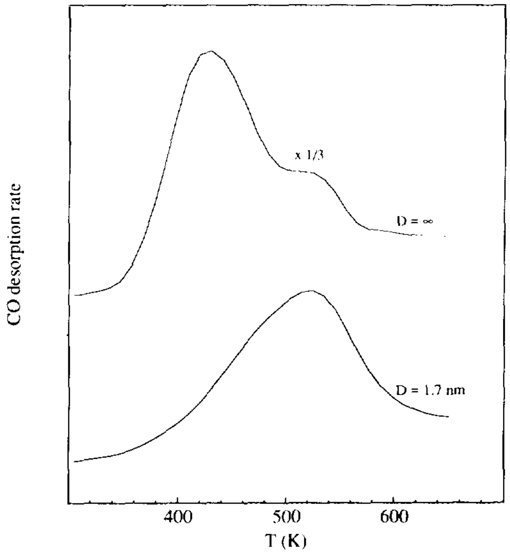

FIG. 3. CO TPD curves for a saturation coverage on Pt/α-Al_2O_3 (0001) for the particle sizes used in the reaction study. The data are taken from Ref. (*11*).

perfectly using simple, first-order rate expressions and rate parameters which are independent of both surface coverage and temperature. Perhaps the most remarkable finding of this study is that the desorption kinetics measured on clean surfaces under UHV conditions can be extrapolated over such a wide range in the experimental conditions to explain observations made in reaction measurements. It would be very interesting to see if similar conclusions can be reached for other important reactions which are known to be structure sensitive, such as NO reduction by CO on Rh (*28, 29*).

SUMMARY

We have demonstrated that the oxidation of CO by O_2 over Pt is structure sensitive at typical reaction pressures. Changes in the specific rates for small Pt particles compared to larger ones can be explained by the lower desorption rates for CO.

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