Catalysis Letters 37 (1996) 9–13

Determination of the rate limiting step in the oxidation of CO on Pt(111) surfaces

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Received 21 August 1995; accepted 25 October 1995

The kinetic behavior of the oxidation of carbon monoxide on Pt(111) was studied at different temperatures by exposing both oxygen-covered surfaces to molecular CO beams and clean surfaces to $CO + O_2$ mixed beams under ultra-high vacuum (UHV) conditions. Results from the first type of experiments show that on oxygen-covered surfaces the rate for CO_2 production above 400 K is determined by the impinging rate of the carbon monoxide molecules. On clean surfaces the oxidation rate is equally determined by the CO incoming flux as long as the $CO : O_2$ ratio in the $CO + O_2$ mixed beams is low. For high $CO : O_2$ ratios, however, the CO steady-state coverage increases, poisoning the adsorption of oxygen, and slowing down the overall CO_2 production. The rate of surface recombination of CO with oxygen also competes with that of CO adsorption at low temperatures, giving rise to a fairly complex overall dynamic behavior.

Keywords: CO oxidation; surface kinetics

1. Introduction

One of the most difficult problems in kinetic studies of catalytic reactions is the determination of the elementary step that limits the rate of the overall process. Since most catalytic experiments are performed under steady-state conditions, the concentrations of the intermediates on the surface generally adjust themselves so the velocity of all the steps in the mechanism becomes equal. Therefore, in order to measure the kinetic parameters for each individual step and to predict the final kinetic behavior of the system, experiments need to be performed under non-steady-state conditions. Modern ultra-high vacuum techniques can in many instances aid in this endeavor. In this letter we illustrate how the use of molecular beam techniques under vacuum have helped in the study of the oxidation of CO over platinum single crystals.

The catalytic oxidation of carbon monoxide has become both a prototype reaction in surface chemistry studies and an increasingly important reaction in the control of pollutants from combustion processes. Extensive studies performed over the past decades [1–13] have led to the development of a general mechanism for this reaction that applies to a wide variety of transition metal-based catalysts. Such mechanism includes a Langmuir–Hinshelwood step [1,2], and considers the adsorption of CO and O_2 to be molecular and dissociative respectively. The overall mechanism can be summarized as follows:

$$CO(g) + S \rightleftharpoons CO(ad) \qquad K_{CO} = k_1/k_{-1} ,$$

$$O_2(g) + 2S \rightleftharpoons 2O(ad) \qquad K_{O_2} = k_2/k_{-2} ,$$

$$CO(ad) + O(ad) \rightleftharpoons CO_2(g) \quad k_3 ,$$

where S represents an empty site on the surface of the catalyst. In lieu of any specific information on the kinetics of the individual elementary steps, the overall rate for the production of CO_2 may be estimated by using a Langmuir-type model. A series of approximations are included in that model, namely:

(1) all surface sites are considered to be identical;

(2) the gaseous CO and O_2 molecules are assumed to compete for the same adsorption sites;

(3) both CO molecules and oxygen atoms are made to each occupy one site upon adsorption;

(4) the adsorbed species are set to be randomly distributed over the array of sites; and

(5) no interaction is considered between adsorbed species other than reaction.

In addition, a few more assumptions are normally added in the derivation of the final kinetic expression, namely:

(6) diffusion of at least one surface species is set to be fast enough not to contribute to the rate of the overall reaction;

(7) the adsorption and desorption of both CO and O_2 are assumed to be fast enough so the coverages of those species always remain near their equilibrium values during reaction;

(8) the rate determining step for the overall reaction is taken to be the recombination of the adsorbed CO with the surface atomic oxygen; and

(9) the produced CO_2 is believed to adsorb weakly on the surface and to desorb as it forms. This means that its surface coverage is negligible at all times [1,2,4–8].

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Using all those assumptions the final expression for the rate of CO_2 formation becomes:

$$R_{CO_2} = k_3 \theta_{CO} \theta_O = \frac{k_3 P_{O_2}^{1/2} P_{CO}}{(1 + K_{O_2}^{1/2} P_{O_2}^{1/2} + K_{CO} P_{CO})^2} \,. \quad (1)$$

Derivations such as these are generally a good starting point for the analysis of the experimental kinetic data from a given reaction. In the particular case of the oxidation of CO, however, recent studies have shown that many of the assumptions mentioned above do in fact not apply [7,8]. This makes eq. (1) invalid, and leads to the need for an alternative kinetic model. In this paper we present results from isothermal kinetic studies on the CO + O reaction which permit the direct evaluation of the validity of most of the assumptions enumerated before and lead to the development of more appropriate rate equations for different specific reaction conditions. The information reported here not only corroborates but also complements earlier published results [15]; the differences between our and previous work is briefly discussed at the end of the paper.

2. Experimental

In this letter we report results from experiments aimed at the determination of the slow step for the oxidation of CO on Pt(111) surfaces. The experiments were performed in a stainless steel ultra-high vacuum (UHV) chamber evacuated with a 300 ℓ/s turbo-molecular pump to a base pressure of 3×10^{-10} Torr (1 Torr = 133.3 N/m^2). This chamber was equipped with a quadrupole mass spectrometer, an effusive molecular beam doser, a sputtering ion gun, and a sample holder capable of three-dimensional translation and on-axis rotation for sample positioning [14]. A collimated multi-channel micro-capillary beam doser 1.2 cm in diameter was used to provide a homogeneous beam across the crystal surface, and a movable flag located between the doser and the surface was employed to start and interrupt the surface exposure to the beam at will. The mass spectrometer was placed far away from the dosing region in order to avoid any possible experimental artifacts due to the angular dependence of the desorption from the surface [15]. The time dependence of the partial pressures of the gases of interest were recorded during the experiments by using an interfaced personal computer.

The Pt(111) crystal (0.9 cm in diameter) was prepared in the usual manner and cleaned in situ by cycles of oxygen dosing at 1100 K, Ar^+ ion sputtering, and annealing at 1200 K before each experiment. The crystal sample could be cooled to liquid nitrogen temperatures and resistively heated up to 1300 K; the temperature was measured by a chromel–alumel thermocouple spot-welded to the back of the crystal.

3. Results and discussion

The kinetics of the oxidation reaction for CO on Pt(111) surfaces was studied under both dynamic and steady-state conditions. These experiments involved the simultaneous recording of the CO uptake and CO_2 evolution rates over time while dosing CO onto oxygen pre-treated surfaces, the measurement of the rates for the steady-state formation of CO_2 while exposing the surface to CO : O_2 pre-mixed beams of different compositions, and the detection of the formation of CO_2 when exposing the clean surface to CO (O_2) beams while maintaining a constant O_2 (CO) background pressure. All these studies were carried out in a temperature range between 100 and 600 K. Absolute incident beam fluxes and CO_2 formation rates were calculated from the raw data by using a calibration procedure discussed in detail in a previous report [14].

As an example of the results obtained by using the first approach, fig. 1 displays the temporal changes in CO and CO_2 partial pressures seen during the dosing of CO on clean and oxygen pre-treated Pt(111) surfaces at different surface temperatures. The oxygen-covered surfaces (O-Pt(111) thereafter) were prepared by exposing the clean Pt(111) crystal to 200 L (1 L = 1×10^{-6} Torr s) of oxygen at 600 K, a procedure that yields a 0.25 ML (1 ML = $1.5 \times 10^{15}/cm^2$) ordered p(2 × 2) oxygen layer [16–19]. For the dosing experiments the CO beam was first set to a pre-determined flux and switched on for a few seconds to let the background CO pressure rise to a steady-state value. The beam blocking flag was then removed at time zero in order to expose the surface directly to the CO beam. As shown in fig. 1, this flag removal induces a drop in the CO partial pressure because of the removal of a significant fraction of the molecules from the gas phase upon adsorption. After the CO pressure returned to its steady-state value, the flag was moved back to the blocking position and the beam was switched off. The raw data displayed in fig. 1 can be easily processed to obtain the desired kinetic data by making use of the fact that the drop in CO partial pressure at any given time is proportional to the sticking coefficient at that instance and the accumulated area of the dip is proportional to the surface coverage at that time [14].

It can be seen from fig. 1 that at 170 K the CO uptake on the clean surface (top trace) follows a precursor mediated kinetics, where the sticking probability has a high and nearly constant value of about 0.8 which persists up to a coverage of around 0.40 ML and then decreases steadily to zero at saturation (approximately 0.60 ML) [14]. Pre-treatment of the surface to oxygen does not significantly affect the CO sticking coefficient in the first stages of the adsorption, but it does reduce the final CO saturation coverage by about a factor of two (middle trace). No CO_2 evolution at all was seen during the uptake experiments at these low temperatures, but

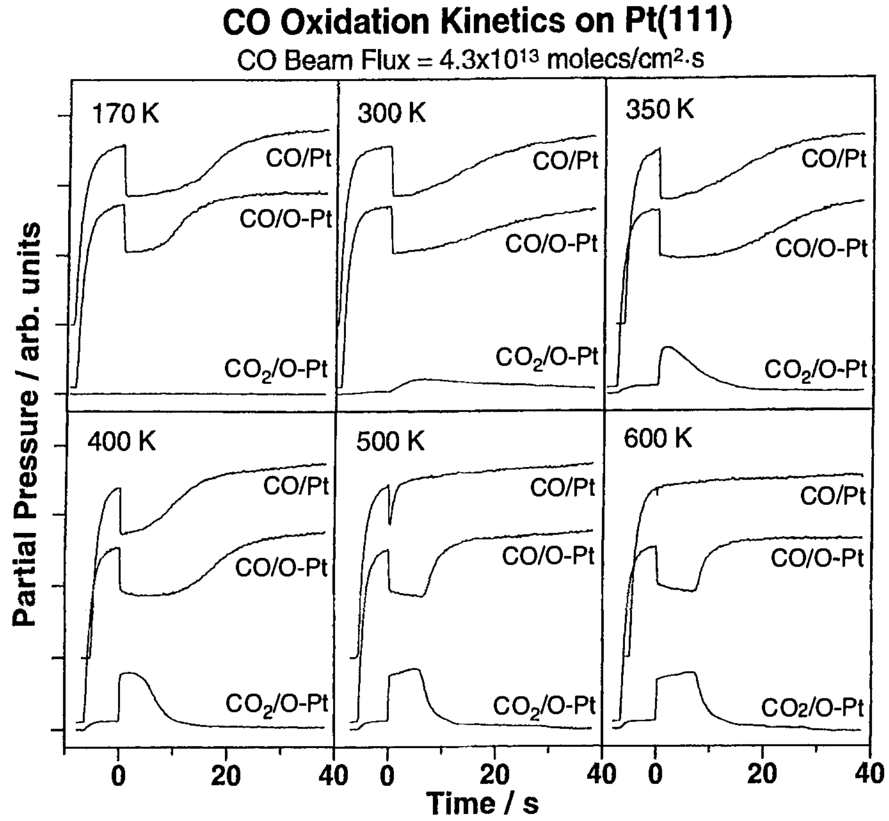

Fig. 1. CO uptake on clean Pt(111) (top), and CO uptake (middle) and CO_2 evolution rates (bottom) on oxygen-covered Pt(111) surfaces at various surface temperatures. The impinging CO flux was fixed at a constant value of 4.3×10^{13} molecules/(cm^2 s) in all cases.

subsequent thermal activation of the resulting CO and oxygen-covered surfaces did lead to the desorption of some CO_2 at 320 K (not shown), as in regular thermal desorption experiments [10].

As the temperature at which the surface is held during the CO beam dosing experiments is raised, the amount of CO adsorption on the O-Pt(111) surface increases relative to that on the clean surface. At 300 K both uptake traces become nearly the same, and at even higher temperatures the *apparent* sticking coefficient for CO on the oxygen-covered surface remains high for longer times than on the clean substrate (see, for instance, the data for 350 K). This is explained by the fact that on the pre-dosed surface the incoming CO reacts with the surface oxygen atoms to form CO_2 during the first stages of the dosing, keeping the CO coverage low until all the oxygen is consumed. The CO_2 that evolves from the surface can be seen in the CO_2 traces displayed in the bottom of each panel of fig. 1.

At surface temperatures above 350 K the decrease in the CO apparent sticking probability on the clean surface becomes even more noticeable, until reaching a point where virtually no net CO adsorption is seen in the uptake traces (above 500 K). This apparent reduction in sticking probability comes about because in this temperature regime the adsorption of CO competes with its desorption, which is activated. On the O-Pt(111) surface, however, there is still considerable CO uptake even at 600 K; in fact, the CO apparent sticking probability at this temperature increases somewhat over time as the incoming CO reacts with the surface oxygen. In addition, the CO_2 signal, which reflects the rate of recombination of the adsorbed CO with the surface oxygen, parallels the uptake behavior seen for CO, and the total number of CO_2 molecules formed (the area under the CO_2 trace) equals both the number of CO molecules consumed and the number of oxygen atoms initially present on the surface (0.25 ML). All these observations point to the fact that in this temperature regime the surface reaction rate is approximately equal to the rate of CO adsorption, while CO desorption is much slower. In other words, the surface reaction rate constant is much larger than those associated with both CO adsorption and desorption. This means that the CO_2 formation rate is governed by the latter step; only after most of the adsorbed oxygen has reacted does the overall rate become roughly proportional to the number of oxygen atoms that remain on the surface.

The fact that the rate limiting step for the oxidation of CO on Pt(111) at high temperatures is the arrival of the CO molecules to the surface can also be seen in the data obtained for the initial rate of CO_2 formation on O-Pt(111) surfaces as a function of CO impinging rate. Fig. 2 provides an example of the results obtained from this type of experiments for a substrate temperature of 600 K where the two rates are shown to be proportional

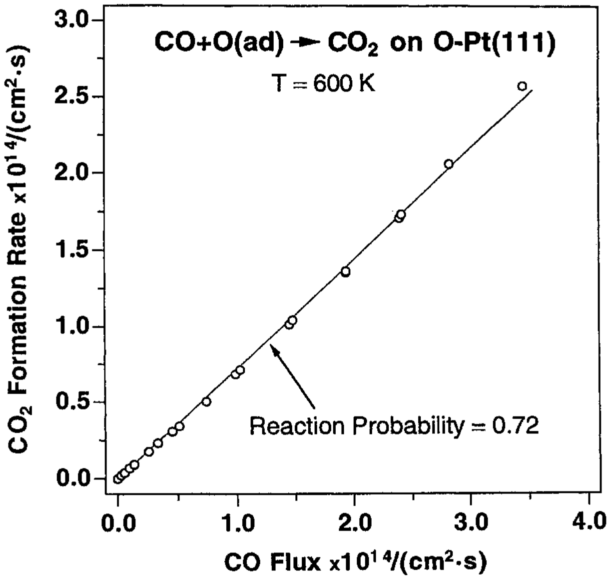

Fig. 2. Initial CO_2 formation rates at 600 K versus impinging CO beam flux on oxygen pre-saturated Pt(111) surfaces.

to each other. The proportionality constant, which represents the initial reaction probability (or the initial apparent sticking probability of CO on the O-Pt(111) surface), was calculated to be 0.72 ± 0.05. This result is consistent with the initial sticking probability for CO adsorption on O-Pt(111) surfaces estimated from the corresponding CO uptake curve in fig. 1 (about 0.8, as mentioned above).

CO oxidation reaction rates were also measured by dosing the clean Pt(111) surface with $CO + O_2$ premixed beams. Fig. 3 displays the steady-state CO_2 formation rate obtained as a function of the $CO : O_2$ ratio in a fixed total-flux beam for three different surface temperatures. For $CO : O_2$ ratios below 10% the CO_2 formation rate was found to be the same for temperatures between 400 and 600 K, and to increase linearly with increasing CO flux. These results corroborate that under CO starving conditions the CO_2 formation rate is limited by the supply of CO, and that the surface oxygen does not inhibit the adsorption of CO. An apparent temperature-independent CO sticking probability of 0.82 ± 0.10 was calculated from the linear relationship between the CO_2 formation rate and the CO impinging rate for $CO : O_2 < 0.1$, again in agreement with the previous data. The CO_2 formation rate does reach a maximum at a given $CO : O_2$ ratio, after which it steadily decreases. This eventual rollover in the CO_2 production rate at high $CO : O_2$ ratios is due to the inhibition in oxygen dissociative adsorption induced by the CO chemisorbed on the surface [1,2]. Experiments where one gas was dosed with the collimated beam doser while the surface was exposed to a background pressure of the other reproduced the results from the experiences with the pre-mixed beams.

The data presented in this paper indicate that several of the assumptions made in deriving eq. (1) do not hold under most reaction conditions. For one, fig. 1 clearly shows that CO does not compete for the same adsorption sites as those occupied by the oxygen atoms (assumptions 1 and 2), since the initial CO uptake is not significantly modified by the previously adsorbed oxygen (only a decrease of about 10% in the initial sticking coefficient for CO is seen at high temperatures). The oxygen uptake, on the other hand, must be inhibited by the adsorbed CO molecules, because the CO_2 production rate goes through a maximum and decreases at high $CO : O_2$ ratios (fig. 3). Also, under CO starving conditions and at temperatures above 400 K, the rate determining step for the oxidation of CO on Pt(111) is the adsorption of CO, not the surface recombination of CO with oxygen atoms on the surface (assumption (8)). Finally, CO adsorption is not in equilibrium with its desorption in this regime (assumption (7)), because the formation of CO_2 is much faster than any of the other steps. The CO surface coverage is kept quite low under these conditions, and since the rate limiting step of the overall reaction is the adsorption of CO,

$$R_{CO_2} = S_{CO}F_{CO} = k_1P_{CO}\,, \tag{2}$$

where S_{CO} is the initial CO sticking probability and F_{CO} its impinging rate. This equation does quantitatively describe the experimental results shown in figs. 2 and 3, and is consistent with the fact that the CO_2 formation rate is independent of the surface temperature at low $CO : O_2$ ratios; sticking probabilities do in general display a weak dependence on surface temperature.

The kinetics of the CO oxidation reaction has already been studied in great detail in the past. Campbell et al. in particular have performed experiments similar to ours, and have reached conclusions that in general agree with ours [15]. However, since their experiments were

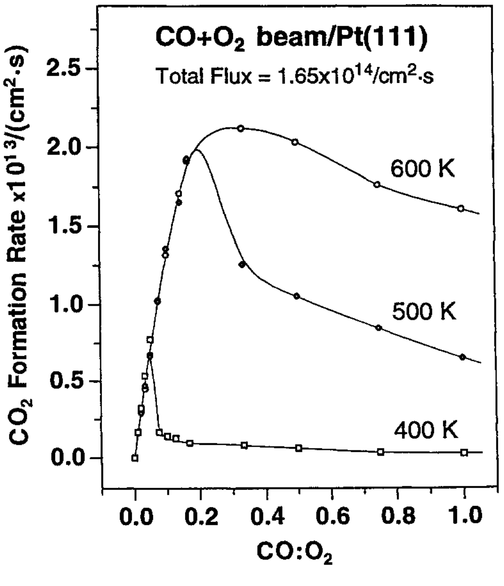

Fig. 3. Steady-state CO_2 formation rates on clean Pt(111) surfaces as a function of $CO : O_2$ ratio for impinging beams with a fixed total $CO + O_2$ flux of 1.65×10^{14} molecules/(cm^2 s). Data is presented for 400, 500, and 600 K surface temperatures.

designed to obtain detailed information about the angular dependence of both the scattered CO and the desorbing CO_2 during the reaction, they were not ideally suited for integrated rate measurements. Here we have been able to accurately measure CO uptake and CO_2 production rates simultaneously as a function of time. This in turn has allowed us to compare the two rates directly and to determine the fraction of the chemisorbed CO molecules that react with the surface oxygen at all times. The ability to perform both measurements simultaneously and accurately is particularly important in the intermediate (300–400 K) temperature regime, where not all the surface oxygen gets consumed by the reaction [20].

Finally, the data presented here also highlight the fact that the rate limiting step for the oxidation of CO changes with reaction conditions. For instance, fig. 1 shows that between 300 and 400 K the kinetics of this process is dominated by the rate of the surface recombination step, not by the CO impinging rate as is the case above 400 K. The rate law for the former step has proven to be quite complex, because it depends not only on the coverages of the reactants but also on their spatial distribution on the surface [20]. A different kinetic behavior was also seen at high CO : O_2 ratios (fig. 3), where the CO chemisorbed on the surface inhibits the adsorption of oxygen [1,2]. A full analysis of the data for these regimes will be published separately [21].

Acknowledgement

Partial financial support for this research was provided by a grant from the Department of Energy. Additional support was provided by Los Alamos National Laboratory through the Los Alamos–University of California Collaborative Research (LACOR) Program.

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