# Distinctive Roles of Chemisorbed Atomic Oxygen and Dioxygen in Methane Catalytic Oxidation on Pt{110}

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The isothermal oxidation of  $C_a$  formed by CH<sub>4</sub> dissociation has been studied on Pt{110} using molecular beam techniques at a surface temperature of 650 K. The reaction products CO and CO<sub>2</sub> are produced in the ratio of 9:1, respectively, for all carbon coverages studied (0.03–0.8 ML). When the O<sub>2</sub> beam is turned on, there is a sharp rise in the rate of CO production (less than 0.1 s) which is attributed for the first time to the surface reaction of C<sub>a</sub> with short-lived chemisorbed molecular dioxygen, O<sub>2c</sub>. This is followed by a slow rise to a maximum rate that is due to the surface reaction between C<sub>a</sub> and adsorbed atomic oxygen, O<sub>a</sub>, which accumulates more slowly on the surface. The initial rate of CO formation from O<sub>2c</sub> decreases as the C<sub>a</sub> precoverage is increased, while the time taken to reach the maximum in the rate from the C<sub>a</sub> + O<sub>a</sub> reaction increases. The CO rate maximum always occurs earlier than that of CO<sub>2</sub>, for all carbon coverages. The rate constant for the C<sub>a</sub> + O<sub>2c</sub> reaction decreases by a factor of 6 up to a C<sub>a</sub> precoverage of 0.2 ML and then stays almost constant up to saturation.

### 1. Introduction

A detailed understanding of the oxidation of carbon over transition-metal surfaces is important for several reasons. First, the surface oxidation of carbon to CO is an important step in the partial oxidation of methane to syngas (CO and  $H_2$  in the ratio 1:2). Second, coke formation during the oxidation of  $C_2$ hydrocarbons leads to catalyst deactivation, a problem which must be avoided for an efficient route to oxidation.

Carbon deposition has been investigated over many metals such as Fe, Ni, and Au.<sup>1-3</sup> Somorjai and co-workers<sup>4</sup> found that over Pt{111} graphite was produced during the decomposition of ethene at high surface temperatures (greater than 850 K). Using XPS, AES, and STM, Kvon et al.5-8 have studied carbon on the Pt{110}-(1 $\times$ 2) surface formed by exposure to residual gases and ethene decomposition. They found that the nature of the adsorbed carbon, C<sub>a</sub>, was dependent on both C<sub>a</sub> coverage and sample temperature. They observed two different temperature regimes. At surface temperatures less than 800 K,  $C_a$  was found to induce the  $(1 \times 2) \rightarrow (1 \times 1)$  structural transformation and was extremely reactive to O<sub>2</sub>. The second type of carbon observed by Kvon et al. was formed when ethene was dosed at 1150 K. In this case, they concluded that the C<sub>a</sub> was "diamond-like" and was extremely unreactive to both H<sub>2</sub> and O<sub>2</sub> below 1100 K. They also studied the adsorption site of the low-temperature reactive  $C_a$ . At coverages,  $\theta$ , of less than  $\sim 0.1$  ML, the C<sub>a</sub> atoms were thought to be located at "near top Pt sites" on the  $(1 \times 1)$  surface, while at higher coverages, 0.3  $\leq \theta \leq 1$  ML, the C<sub>a</sub> dissolved into the surface via a carbide state. They also found that even at a  $C_a$  coverage of ~0.1 ML, the coverage estimated from STM data was significantly less than that measured using AES, which suggested that some of the carbon was just beneath the surface. In fact, DFT slab calculations performed in our group by Petersen et al.<sup>9</sup> for C<sub>a</sub> on  $Pt{110}-(1\times 2)$  and  $Pt{110}-(1\times 1)$  show that a pseudo-4fold site with the Ca atom located just below the surface was the most stable.

While catalytic C<sub>a</sub> oxidation has been studied extensively, very little work has been done on single crystals. In all cases, the products were found to be CO<sub>2</sub> and CO, the selectivity being a complex function of the surface temperature, O<sub>a</sub> coverage, and reaction temperature used. Schäfer and Wassmuth<sup>10</sup> studied the oxidation of graphite on Pt{111} over a surface temperature range of 550-1100 K. They found that oxidation yields CO<sub>2</sub> (500-800 K) and CO (700-1100 K) as the desorbing reaction products. They explained the temperature-dependent selectivity using a model where O<sub>a</sub> and CO<sub>a</sub> were highly mobile while C<sub>a</sub> atoms were immobile and the mean residence time of CO<sub>a</sub> decreased with increasing surface temperature. Walker and King<sup>11</sup> studied the oxidation of C<sub>a</sub>, formed by CH<sub>4</sub> decomposition, on Pt{110}-(1 $\times$ 2) over the temperature range 550-750 K. They observed that the percentage of  $CO_2$  produced in the  $CO_2+CO$  product decreases from ~50% to less than 1% when the surface temperature is increased from 550 to 750 K, and that the  $CO_2$  peak maximum occurs later than that of CO.

The underlying mechanism of oxidation is still a matter of much debate. On Rh foil, using AES and XPS, Mikhailov et al.12 found that the reaction was Langmuir-Hinshelwood, in which both the Oa and Ca atoms were thermally equilibrated with the surface. Walker and King<sup>11</sup> concluded that on Pt{110}-(1×2) two processes are operative, a Langmuir-Hinshelwood mechanism between Oa and Ca and a reaction between C<sub>a</sub> and chemisorbed molecular dioxygen, O<sub>2c</sub>, in which CO formed in the surface reaction at high surface temperatures is impulsively desorbed. The spatial distribution of the impulsively desorbed CO shows a sharp lobe centered at an angle of 32° from the surface normal. The CO translational energy was estimated from the shape of the distribution to be  $\geq 135 \pm 5$  kJ mol<sup>-1</sup>. Kislyuk et al.<sup>13</sup> had previously reported a slightly peaked distribution along the surface normal on Pt foil. However, Walker and King also concluded that as the surface temperature is lowered, between 650 and 500 K, the CO formed in the surface reaction between O<sub>2C</sub> and C<sub>a</sub> is no longer promptly desorbed: it is trapped into the chemisorbed CO<sub>a</sub> state.

The second product, CO<sub>2</sub>, is produced by the reaction of equilibrated adsorbed CO, with  $O_a$ .<sup>11</sup> This reaction has been well studied<sup>14–16</sup> on Pt{110}-(1×2). The general consensus is that CO<sub>2</sub> desorbs with excess energy.<sup>17,18</sup>

In this paper, we extend the  $C_a$  coverage range on Pt{110} studied by Walker and King<sup>11</sup> and find that for all surface carbon coverages studied,  $C_a$  is oxidized to CO and CO<sub>2</sub> in a ratio of 9:1. We proceed to examine the mechanism of  $C_a$  oxidation in detail.

#### 2. Experimental Details

The experimental apparatus is described in detail elsewhere.<sup>19</sup> The sample is mounted centrally on a manipulator in an ultrahigh vacuum chamber with a base pressure of  $< 2 \times 10^{-10}$  mbar. The molecular beam is sourced at a supersonic expansion from a 50  $\mu$ m nozzle, skimmed, differentially pumped, and collimated before entering the sample chamber. An inert King and Wells (KW) flag just in front of the crystal is used to control the dosing time and to measure sticking probabilities.<sup>20</sup> A further flag in the source stage allows the beam to be turned on and off. The surface temperature ( $T_s$ ) is monitored by a crystal-mounted thermocouple referenced to an electronic ice-point and is regulated by programmed resistive heating. The partial pressures of up to 16 individual gases can be monitored using a fixed QMS situated behind the crystal.

The Pt sample, 11 mm diameter by 1 mm thick, was cut to within 0.1° of the {110} plane. Initial cleaning of the crystal was achieved by repeated cycles of ion sputtering, annealing, and oxygen treatment. Routine cleaning consisted of annealing at 1240 K, exposure to oxygen for 5 min while cooling from 1100 to 950 K, and annealing for 15 min at 950 K. This procedure yields a clean  $Pt{110}-(1\times 2)$  surface which gives a sharp LEED pattern and oxygen thermal desorption spectra that are in good agreement with the literature.<sup>21</sup> It should also be noted that Auger analysis performed during earlier studies found no evidence for impurities such as calcium, sulfur, and silicon, and the above cleaning procedure removed carbon which remained on the surface after experiments. The CH<sub>4</sub> and O<sub>2</sub> used were > 99.9995% and 99.995% pure, respectively, as quoted by the suppliers (Messer (U.K.) Ltd.). The supersonic methane beams used in these experiments to prepare the  $CH_a$ adlayers had a composition of 8% CH-92% He, and the nozzle was heated to 790 K. The oxygen beam used was produced using a room-temperature nozzle. All coverages are quoted in monolayers (ML) (1 ML  $\equiv$  9.22×10<sup>14</sup> molecules cm<sup>-2</sup>) and were determined using the spinning rotor gauge which measures absolute beam fluxes and by comparison of TPD areas with earlier studies.22,23

#### 3. Results and Discussion

Carbon buildup can become a problem during the oxidation of higher weight hydrocarbons on metal surfaces. To gain some insight into this important problem, we have now studied the oxidation of  $C_a$  on Pt{110}-(1×2) at high coverages at a surface temperature of 650 K. The  $C_a$  adlayers were prepared by dosing the He-seeded CH<sub>4</sub> beam for different amounts of time at a surface temperature of 650 K. The temporal profiles of the two products, CO and CO<sub>2</sub>, are shown in Figures 1 and 2, respectively, whereas the corresponding O<sub>2</sub> reactive sticking probabilities are shown in Figure 3. For the lowest  $C_a$  coverage (0.03 ML), the CO<sub>2</sub> and CO peak shapes are identical to those reported by Walker and King,<sup>11</sup> whose experiments were performed with a  $C_a$  coverage of 0.01 ML. There is a sharp initial rise in the CO pressure followed by a slow rise to the



Figure 1. CO produced by the isothermal reaction of different  $C_a$  precoverages with an 0.014 ML s<sup>-1</sup> O<sub>2</sub> molecular beam at a surface temperature of 650 K. The carbon precoverages were as shown in the legend.



Figure 2.  $CO_2$  produced by isothermal reaction of different  $C_a$  precoverages with an 0.014 ML s<sup>-1</sup> O<sub>2</sub> molecular beam at a surface temperature of 650 K. The carbon precoverages were as shown in the legend.



**Figure 3.** Reactive  $O_2$  sticking probability during the isothermal reaction of adsorbed carbon with a  $O_2$  molecular beam at a surface temperature of 650 K. The  $O_2$  beam flux was 0.014 ML s<sup>-1</sup>, and the  $C_a$  precoverages were as shown in the legend.

maximum while the  $CO_2$  maximum occurs after that of the CO, the details of which will be discussed later.

We deal with the CO production first. As the  $C_a$  precoverage increases, the extent of the height of the initial sharp rise in the CO pressure (the prompt process) decreases, and the time taken to reach the maximum increases. In fact, for the highest  $C_a$ coverage (0.83 ML), the prompt rise is small, and it takes 340 s for the CO production rate to reach a maximum. It should be noted that for the highest coverages studied, not all the  $C_a$  could be reacted off at 650 K, and the surface temperature had to be increased to greater than 1000 K to remove totally the  $C_a$  by oxidation.

The temporal profiles of the  $CO_2$  production are presented in Figure 2. The peak maximum for each  $C_a$  precoverage occurs at a later time than the corresponding CO peak maximum. The



**Figure 4.** Initial reactive sticking probability of an O<sub>2</sub> beam of 0.014 ML s<sup>-1</sup> as a function of C<sub>a</sub> coverage relative to saturation at a surface temperature of 650 K. The solid line is  $s_0(1 - \theta_C/\theta_{sat})^2$ .

 $O_2$  flux (0.014 ML s<sup>-1</sup>) used in these experiments was considerably higher than that used by Walker and King,<sup>11</sup> which results in measurable CO<sub>2</sub> production as soon as the KW flag is raised. The time-dependent reactive O<sub>2</sub> sticking probability is shown in Figure 3. From run to run, the initial O<sub>2</sub> sticking probability decreases with increasing C<sub>a</sub> precoverage while the time-dependent sticking probability increases to a maximum as the C<sub>a</sub> is removed during the reaction and then decreases to about 0.03, for all C<sub>a</sub> precoverages. The decrease is attributed to an increasing surface coverage of Oa. The maximum in the O<sub>2</sub> reactive sticking probability coincides with the maximum in the CO<sub>2</sub> production rate for a given C<sub>a</sub> precoverage. The magnitude of the maximum reactive sticking probability is also interesting. For the lowest two Ca precoverages, the maximum is  $\sim 0.225$ , which is the sticking probability on the clean surface at 650 K.<sup>21</sup> This implies that the total surface coverage ( $C_a$ , CO<sub>a</sub>, and O<sub>a</sub>) is very low at this stage. For the two higher C<sub>a</sub> precoverages, the maximum sticking probability is reduced to 0.19 and 0.175, respectively. When oxidation is complete at these precoverages, there is still some unreactive graphitic carbon left. This acts as a site blocker and explains the reduced maximum sticking probability.

Figure 4 shows the initial reactive sticking probability as a function of the C<sub>a</sub> precoverage. The sticking probability decreases according to  $s_0(1 - \theta_C/\theta_{sat})^2$ , where  $s_0$  is the initial sticking probability on the clean surface at 650 K and  $\theta_C/\theta_{sat}$  is the carbon coverage relative to the saturation C<sub>a</sub> coverage at a surface temperature of 650 K.

The lowering of the initial  $O_2$  sticking probability with increasing  $C_a$  precoverage shows that  $C_a$  acts as a site blocker to  $O_2$  adsorption and that  $O_2$  must first chemisorb, either molecularly or dissociatively, before reaction with  $C_a$  can take place. If the reaction occurred via an Eley–Rideal mechanism involving a collision of a gaseous  $O_2$  with  $C_a$ , the initial rate would increase as the  $C_a$  precoverage increases; in fact the opposite is true. Walker and King<sup>21</sup> have shown that on Pt{110}-(1×2) dissociative oxygen adsorption occurs via chemisorbed molecular dioxygen,  $O_{2c}$ . Therefore, the reaction to produce CO may occur by reaction of  $C_a$  with either or both types of chemisorbed oxygen.

Walker and King<sup>11</sup> have shown that two processes are operative during the oxidation of  $C_a$  at low coverages: in the first,  $C_a$  reacts with the short-lived but highly mobile  $O_{2c}$  to produce CO which at 650 K impulsively desorbs in a sharp lobe at an angle of 32° to the surface normal (the initial sharp rise); The second is a Langmuir—Hinshelwood (LH) reaction between  $C_a$  and  $O_a$  (the slower rise to a maximum). They found that the CO produced via the reaction of  $C_a$  with  $O_{2c}$  has excess translational energy greater than 135 kJ mol<sup>-1</sup>, and is therefore

not equilibrated with the surface before desorption, at a surface temperature of 650 K. On the other hand, CO produced by the Langmuir–Hinshelwood reaction of  $C_a$  with  $O_a$  has excess energy of 20 kJ mol<sup>-1</sup> and is equilibrated with the surface before desorption or reaction with  $O_a$  to produce CO<sub>2</sub>, which explains the delayed maximum in CO<sub>2</sub> production.

The temporal profiles obtained at the lowest carbon coverages (Figures 1 and 2) are identical to those obtained by Walker and King.<sup>11</sup> However, to determine whether our experimental data obtained at higher  $C_a$  precoverages are consistent with their mechanism, we consider the following set of equations which describe the processes taking place at the surface in more detail:

$$O_2(g) \xrightarrow[k_d]{\alpha F_{02}} O_{2c} \xrightarrow{k_a} 2O_a$$
 (1)

$$C_{a} + O_{2c} \xrightarrow{k_{CO}^{*}} CO_{g}^{*} + O_{a}$$
 (2)

$$C_{a} + O_{2c} \xrightarrow{k_{COg^{*}}} CO_{a} + O_{a}$$
(3)

$$C_a + O_a \xrightarrow{k_{CO}} CO_a$$
 (4)

$$\operatorname{CO}_{a} \xrightarrow{k_{des}} \operatorname{CO}_{g}$$
 (5)

$$CO_a + O_a \xrightarrow{k_{CO_2}} CO_2(g)$$
 (6)

Here,  $\alpha$  and  $F_{O_2}$  are the O<sub>2</sub> trapping probability and O<sub>2</sub> flux, respectively, and CO<sub>g</sub>\* is the translationally hot gas-phase product of the C<sub>a</sub> + O<sub>2c</sub> reaction. The first step (eq 1) involves the dissociation of O<sub>2</sub> via chemisorbed molecular dioxygen, O<sub>2c</sub>, which can react with C<sub>a</sub> to produce CO which impulsively desorbs (eq 2) or at surface temperatures lower than 650 K can be trapped and equilibrated to produce CO<sub>a</sub> (eq 3). Any O<sub>2c</sub> which dissociates before reacting or desorbing forms O<sub>a</sub> which reacts with C<sub>a</sub> to produce CO<sub>a</sub> (eq 4). The CO<sub>a</sub> can then either desorb or be oxidized to CO<sub>2</sub> via two competing pathways (eqs 5 and 6).

The above equations can be used to obtain the following expression for the rate of change of  $\theta_{O2c}$ ,  $\theta_{Oa}$  and  $\theta_{Ca}$ , respectively:

$$\frac{\mathrm{d}\theta_{\mathrm{O2c}}}{\mathrm{d}t} = \alpha(\theta_{\mathrm{Ca}}, \theta_{\mathrm{O_a}})F_{\mathrm{O2}} - k_{\mathrm{d}}\theta_{\mathrm{O_{2c}}} - k_{\mathrm{a}}\theta_{\mathrm{O_{2c}}} - k_{\mathrm{CO}}^*\theta_{\mathrm{O_{2c}}}\theta_{\mathrm{C_a}}$$
(7)

$$\frac{\mathrm{d}\theta_{\mathrm{O}_{a}}}{\mathrm{d}t} = 2k_{\mathrm{a}}\theta_{\mathrm{O}_{2c}} + k_{\mathrm{CO}}^{*}\theta_{\mathrm{O}_{2c}}\theta_{\mathrm{C}_{a}} - k_{\mathrm{CO}}\theta_{\mathrm{C}_{a}}\theta_{\mathrm{O}_{a}} - k_{\mathrm{CO}_{2}}\theta_{\mathrm{CO}_{a}}\theta_{\mathrm{O}_{a}}$$
(8)

$$\frac{d\theta_{\rm Ca}}{dt} = -k_{\rm CO}^* \theta_{\rm O_{2c}} \theta_{\rm C_a} - k_{\rm CO} \theta_{\rm C_a} \theta_{\rm O_a} \tag{9}$$

The trapping probability of O<sub>2</sub> into the molecular chemisorbed state is a function of both  $\theta_{C_a}$  and  $\theta_{O_a}$  and is expressed as  $\alpha$ - $(\theta_{C_a}, \theta_{O_a})$ .

Chemisorbed molecular oxygen,  $O_{2c}$ , desorbs and dissociates at 160 K. The lifetime of  $O_{2c}$  on the surface is given by  $\tau = \tau_0 \exp(E_d/RT_s)$  where  $E_d$ , the desorption energy, is ~60 kJ mol<sup>-1</sup>.<sup>21</sup> Assuming that  $1/\tau_0$  is the vibrational frequency of the particle-surface bond (about 860 cm<sup>-124</sup>), the lifetime of  $O_{2c}$  is about 2 ns at 650 K. Therefore, at any time significantly longer than this  $d\theta_{O_{2c}}/dt = 0$  and  $\theta_{O_{2c}}$  is given by

$$\theta_{O_{2c}} = \frac{\alpha(\theta_{C_a}, \theta_{O_a}) F_{O_2}}{k_d + k_a + k_{CO}^* \theta_{C_a}}$$
(10)

We have shown earlier that CO production is best described as a combination of a fast process and a slower LH reaction between  $C_a$  and  $O_a$ . Therefore, the total rate of gaseous CO produced,  $r_{CO_{TOT}}$  is given by

$$r_{\rm CO_{TOT}} = r_{\rm CO}^* + r_{\rm CO} \tag{11}$$

where  $r_{CO}^*$  and  $r_{CO}$  are the rate of CO production by via the impulsive and LH mechanisms, respectively. Since the pumping speed is high,  $r_{CO_{TOT}}$  is proportional to CO pressure measured by the fixed QMS,  $P_{CO_{TOT}}$ . The QMS response to different gases has been calibrated and can therefore be directly related to the production rate. The rate of gaseous CO formation via each pathway is given by

$$r_{\rm CO}^* = k_{\rm CO}^* \theta_{\rm O_2} \theta_{\rm C_2} \tag{12}$$

$$r_{\rm CO} = k_{\rm CO} \theta_{\rm O_a} \theta_{\rm C_a} - k_{\rm CO_2} \theta_{\rm CO_a} \theta_{\rm O_a}$$
(13)

This equation was obtained by assuming that as soon as CO is produced by the LH mechanism it either desorbs immediately or reacts with another  $O_a$  to produce  $CO_2$  ( $C_a$  oxidation is the rate-determining step for gas-phase CO production).

Using mass balance, we determined  $\theta_{\rm C}$  and  $\theta_{\rm O}$  during the reaction of carbon with an O<sub>2</sub> molecular beam at C<sub>a</sub> precoverages of 0.18 and 0.83 ML, as shown in Figures 5 and 6, respectively. First, for the low C<sub>a</sub> precoverage experiment, the  $O_{2c}$  coverage, which is given by eq 10, initially rises to the steady-state value (less than 0.1 s), stays almost constant, and then decreases as the Oa coverage builds up. Since the production of impulsive CO is proportional to the product of the O<sub>2c</sub> and the C<sub>a</sub> coverage, the production rate very rapidly reaches the maximum at  $t \simeq 0$  and decreases at a similar rate to that of the decrease in carbon coverage. On the other hand, the O<sub>a</sub> coverage initially rises slowly, with a sharper rise after 32 s. This is consistent with the maximum rate of the Langmuir-Hinshelwood Ca + Oa reaction occurring after about 30 s, as observed (see inset Figure 5). Because the surface temperature is much higher than the desorption temperature of CO, 525 K,<sup>25</sup> CO desorbs very rapidly once it has formed. In order for CO<sub>2</sub> to form from CO<sub>a</sub> and O<sub>a</sub>, there must be a large surface oxygen coverage. Thus, the rate of CO<sub>2</sub> formation only becomes significant once the coverages of O<sub>a</sub> increase. The coverage curves are therefore consistent with the idea that we have two competing mechanisms taking place.

The behavior is quite different for the high coverage experiment, as shown in Figure 6. Again the maximum in the impulsive CO formation rate occurs at t = 0. The initial rate is significantly less due to the reduced steady-state O<sub>2c</sub> coverage (C<sub>a</sub> acts as a site blocker). The O<sub>a</sub> coverage, however, rises slowly to a maximum with a curvature typical of a clean-off reaction and shows that the reaction with atomic oxygen dominates when high C<sub>a</sub> precoverages are used.

#### 4. Variation of k\*<sub>CO</sub> with C<sub>a</sub> Coverage

At the beginning of the reaction (as  $t \rightarrow 0_s$ ),  $\theta_{O_a}$  is very small, whereas  $\theta_{O2c}$  has already reached its steady-state value (after



**Figure 5.** Surface  $O_a$  and  $C_a$  coverages during the reaction of carbon with an  $O_2$  molecular beam at a surface temperature of 650 K. The  $C_a$  precoverage was 0.18 ML, and the  $O_2$  beam flux was 0.014 ML s<sup>-1</sup>. The inset shows the corresponding product and  $O_2$  uptake profiles.



**Figure 6.** Surface  $O_a$  and  $C_a$  coverages during the reaction of carbon with an  $O_2$  molecular beam at a surface temperature of 650 K. The  $C_a$  precoverage was 0.83 ML, and the  $O_2$  beam flux was 0.014 ML s<sup>-1</sup>.

less than 1  $\mu$ s). Therefore, CO is produced exclusively via the impulsive mechanism, and the initial sharp rise in the CO pressure, P<sub>CO</sub>, is given by

$$r_{\rm CO} = cP_{\rm CO} = k_{\rm CO}^* \theta_{\rm O_2} \theta_{\rm C_2} \tag{14}$$

where *c* is a constant related to the pumping speed of the system. The measured initial reactive sticking probability, *s*<sub>r</sub>, multiplied by the O<sub>2</sub> flux is equal to the rate at which O<sub>2c</sub> is consumed which is approximately equal to  $s_0(1 - \theta_C/\theta_{sat})^2$ , as shown in Figure 4.

$$s_{\rm r}F_{\rm O_2} = k_{\rm a}\theta_{\rm O_{2c}} + k_{\rm CO}^{*}\theta_{\rm O_{2c}}\theta_{\rm C_a} \simeq s_0(1-\theta_{\rm Ca})^2 F_{\rm O_2} \quad (15)$$

Substituting this into eq 7 and applying the steady-state approximation gives

$$k_{\rm d}(\theta_{\rm O_{\rm YC}}) = \alpha(\theta_{\rm C_2})F_{\rm O_2} = s_{\rm r}F_{\rm O_2} \tag{16}$$

Since the  $\theta_{\rm C}$  dependence of  $\alpha$  and  $s_{\rm r}$  are the same and the trapping probability is related to the sticking probability according to  $\alpha = s(1 + k_{\rm d}/k_{\rm a})$ , the above expression rearranges to give the following expression for  $\theta_{\rm O2c}$ :

$$\theta_{\mathrm{O}_{2c}} = \frac{s_{\mathrm{r}} F_{\mathrm{O}_2}}{k_{\mathrm{a}}} \tag{17}$$

Inserting this into eq 14 and rearranging gives the final expression for the coverage dependence of  $k_{CO}^*$ , in terms of



**Figure 7.** Plot of  $P_{CO}/(\theta_C s_r F_{O_2})$  versus  $\theta_C$  for the reaction of  $C_a$  with  $O_{2c}$  at a surface temperature of 650 K.

**TABLE 1:** Parameters Used in the Model

reaction	rate (s <sup>-1</sup> )	$E_{\rm a}$ (kJ mol <sup>-1</sup> )	$\nu (s^{-1})$	ref
O <sub>2</sub> flux	F	$0.014 \text{ ML s}^{-1}$		calcd.
$C_a + O_a \rightarrow CO_a$	$k_{\rm CO}$	0	24	а
$CO_a + O_a \rightarrow CO_2(g)$	$k_{\rm CO_2}$	58.6	$2 \times 10^{9}$	b
$CO_a \rightarrow CO(g)$	k <sub>des</sub>	158.8	$2 \times 10^{16}$	С

 $^a$  From previous work.  $^{11\ b}$  From previous works.  $^{14,26\ c}$  From previous works.  $^{25,27,28}$ 

 $P_{\rm CO}$ ,  $s_{\rm r}$ , and  $\theta_{\rm Ca}$  all of which can be determined experimentally:

$$k_{\rm CO}^{*} = \frac{k_{\rm a} P_{\rm CO}}{\theta_{\rm C_{\rm a}} s_{\rm r} F_{\rm O_{\rm c}}}$$
(18)

A plot of  $P_{\rm CO}/(\theta_{\rm CSr}F_{\rm O_2})$  versus  $\theta_{\rm C}$  is shown in Figure 7. This gives  $k_{\rm CO}^*/k_a$  as a function of  $\theta_{\rm Ca}$ . Assuming that  $k_a$  is independent of coverage, this implies that  $k_{\rm CO}^*$  decreases sharply to a coverage of 0.2 ML and remains essentially constant above about 0.4 ML. The most likely reason for this is the C<sub>a</sub>-induced  $(1 \times 2) \rightarrow (1 \times 1)$  transformation.<sup>5–8</sup> At the lowest coverage, the structure is entirely  $(1 \times 2)$ . However, as the coverage increases, C<sub>a</sub> stabilizes the  $(1 \times 1)$  structure which may result in an increased activation energy. In fact, the activation energy only needs to increase by ~3.5 kJ mol<sup>-1</sup> to explain the reduced rate constant.

**4.1. Modeling the**  $C_a + O_a$  **Reaction.** To simulate the experimental observations at high  $C_a$  precoverages, the following elementary reaction steps were assumed:

$$O_2(g) + 2* \xrightarrow{Fs_r} 2O_a \tag{19}$$

$$C_a + O_a \xrightarrow{k_{CO}} CO_a + *$$
 (20)

$$\operatorname{CO}_{a} \xrightarrow{k_{\operatorname{des}}} \operatorname{CO}_{g} + *$$
 (21)

$$\operatorname{CO}_{a} + \operatorname{O}_{a} \xrightarrow{k_{CO2}} \operatorname{CO}_{2}(g) + 2*$$
 (22)

Equation 19 represents  $O_2$  dissociative adsorption on the Pt{110}-C<sub>a</sub> surface. For simplicity, it is assumed that each adsorbate blocks one free site (represented by \*) and that the total number of free sites  $\theta^*$  is equal to  $(1 - \theta_{COa} - \theta_{Ca} - \theta_{Cgra} - \theta_{Oa})$  where  $\theta_{Cgra}$  is unreactive carbon and that each  $O_2$  requires two free sites to dissociate.  $O_2$  desorption is not included because at a surface temperature of 650 K it does not occur to a significant degree. Since the carbon induced  $(1 \times 2) \rightarrow (1 \times 1)$  structural transformation is not well understood we use the parameters reported in the literature for  $CO_a$  oxidation (eq 22)<sup>14,26</sup> and desorption (eq 21).<sup>25,27,28</sup> For the C<sub>a</sub> + O<sub>a</sub> reaction



**Figure 8.** Experimental (solid lines) and modeled (dashed lines) product profiles for the isothermal reaction of  $C_a$  with an  $O_2$  molecular beam, at a surface temperature of 650 K. The products are CO (major product) and CO<sub>2</sub>.

we use the parameter obtained by Walker and King<sup>11</sup> for low precoverages on the same surface. All of the parameters used in the model are shown in Table 1.

It should be noted that in this Langmuir–Hinshelwood model the  $O_a$  is thermally equilibrated with the surface before reaction with the  $C_a$  adlayer takes place. It is a mean field model and so no local information about the structural dependence of the reaction can be included.

Four coupled differential equations are used to describe the variation of the number of free sites and adsorbate coverages:

$$\frac{\mathrm{d}\theta_{\mathrm{O}}}{\mathrm{d}t} = 2sF_{\mathrm{O}_{2}}(\theta^{*})^{2} - k_{\mathrm{CO}}\theta_{\mathrm{C}}\theta_{\mathrm{O}} - k_{\mathrm{CO}_{2}}\theta_{\mathrm{CO}}\theta_{\mathrm{O}} \qquad (23)$$

$$\frac{\mathrm{d}\theta_{\mathrm{C}}}{\mathrm{d}t} = -k_{\mathrm{CO}}\theta_{\mathrm{C}}\theta_{\mathrm{O}} \tag{24}$$

$$\frac{\mathrm{d}\theta_{\mathrm{CO}}}{\mathrm{d}t} = k_{\mathrm{CO}}\theta_{\mathrm{C}}\theta_{\mathrm{O}} - k_{\mathrm{CO}_{2}}\theta_{\mathrm{CO}}\theta_{\mathrm{O}} - k_{\mathrm{d}}\theta_{\mathrm{CO}} \qquad (25)$$

$$\frac{\mathrm{d}\theta^*}{\mathrm{d}t} = -2\mathrm{s}F_{\mathrm{O}_2\theta}^* + k_{\mathrm{CO}}\theta_{\mathrm{C}}\theta_{\mathrm{O}} + k_{\mathrm{d}}\theta_{\mathrm{CO}} + 2k_{\mathrm{CO}_2}\theta_{\mathrm{CO}}\theta_{\mathrm{O}} \quad (26)$$

where  $\theta_x$  and  $\theta^*$  are, respectively, the concentration of species x relative to the carbon saturation coverage and the fraction of sites available for adsorption. The system of coupled differential equations was integrated numerically using routines in the NAG Fortran Library. This program returned time-dependent coverages which were substituted into the following equation to give the time-dependent product profiles for  $P_{CO}$ ,  $P_{CO2}$  and *s*:

$$r_{\rm CO} = cP_{\rm CO} = k_{\rm d}\theta_{\rm CO} \tag{27}$$

$$r_{\rm CO_2} = cP_{\rm CO_2} = k_{\rm CO_2}\theta_{\rm CO}\theta_{\rm O}$$
(28)

$$s = s_0(\theta^*)^2 \tag{29}$$

The experimentally determined and corresponding modeled profiles for the reaction of 0.83 ML  $C_a$  with a 0.014 ML s<sup>-1</sup> O<sub>2</sub> molecular beam at a surface temperature of 650 K can be seen in Figure 8. We get good qualitative agreement, in that the CO pressure rises slowly to a maximum as the reaction proceeds and then decreases sharply near the end of the reaction and the CO<sub>2</sub> peak maximum occurs after that of CO. There are, however, some subtle differences between the experimental and modeled profiles. The initial rate of CO production is significantly larger in the model. The initial CO production rate can be decreased to match the initial rates by making  $k_{\rm CO}$  smaller. However, this

results in the modeled peak maximum occurring at a much later time than that determined experimentally. In this model, we assume however, that  $k_{CO}$  is independent of C<sub>a</sub> coverage, C<sub>a</sub> does not form islands, and the reaction proceeds entirely via a Langmuir-Hinshelwood reaction between Ca and Oa. A more sophisticated model which incorporated all of these effects should give a much better fit to the data. However, the relatively good agreement obtained using such a simple model indicates that the underlying mechanism is essentially correct.

#### 5. Summary and Conclusion

The isothermal reaction of Ca with an O2 molecular beam was studied on Pt{110} at surface temperature of 650 K and over a C<sub>a</sub> coverage range of 0.03-0.8 ML. For all coverages, CO and CO<sub>2</sub> were produced in the ratio of about 9:1. There is an initial sharp rise in the CO pressure which is attributed to the reaction of  $C_a$  with adsorbed molecular oxygen,  $O_{2c}$ , followed by a slow rise to a maximum which is due to the reaction of C<sub>a</sub> with adsorbed atomic oxygen, O<sub>a</sub>. This is the first time that molecular chemsiorbed oxygen has been implicated in the oxidation of adsorbed carbon and, by implication, in the methane partial oxidation reaction. The height of the initial sharp rise in CO pressure decreases as the C<sub>a</sub> precoverage increases while the time taken to reach the maximum also increases. The CO peak maximum occurs earlier than that of  $CO_2$  for all  $C_a$  coverages. This is because the  $CO_2$  formation rate is maximized only when the surface atomic oxygen coverage is large.

The time-dependent surface coverages during the isothermal oxidation at 650 K were obtained using mass balance. By use of the initial O<sub>2</sub> reactive sticking probability, the initial sharp rise in CO pressure and the Ca coverage, the rate constant was obtained for the  $C_a{+}O_{2c}$  reaction as a function of the  $C_a$ precoverage. It decreases by a factor of 6 up to a Ca precoverage of 0.2 ML and then stays almost constant; the change corresponds to an increase of  $\sim 3.5 \text{ kJ mol}^{-1}$  in the activation energy. This change in the activation energy is attributed to a lifting of the  $(1 \times 2)$  reconstruction of the Pt{110} surface to  $Pt{110}-(1\times 1)$  by  $C_a$ .

The profiles for the highest Ca precoverage are quite successfully modeled using a simple Langmuir-Hinshelwood reaction mechanism, where CO is produced by the reaction of  $C_a + O_a$  and  $CO_2$  is produced by the competing  $CO_a + O_a$ reaction. The model gives a reasonable, qualitative fit to the data, which supports the underlying mechanism.

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