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# Kinetics of carbon monoxide oxidation over ruthenium(0001)

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$$a_{xy}^{\text{aniso}}(3) = a_{yx}^{\text{aniso}}(3) = -a_{xy}^{\text{aniso}}(4) = -a_{yx}^{\text{aniso}}(4) = 0.293 \text{ mT}$$

and the total superhyperfine matrix elements become

$$a(2) = \begin{pmatrix} 19.826 & 0 & 0 \\ 0 & 21.177 & 0 \\ 0 & 0 & 19.296 \end{pmatrix}$$

$$a(3) = \begin{pmatrix} 20.839 & 0.293 & 0 \\ 0.293 & 20.164 & 0 \\ 0 & 0 & 19.296 \end{pmatrix}$$

$$a(4) = \begin{pmatrix} 20.839 & -0.293 & 0 \\ -0.293 & 20.164 & 0 \\ 0 & 0 & 19.296 \end{pmatrix}$$

Although the anisotropic contribution is small compared to the isotropic one it is of the order of 1.0 mT. Such splittings are easily detectable in EPR spectra of narrow line widths and certainly detectable in ENDOR experiments. Inspection of the reported EPR spectra of Forbes et al.<sup>2</sup> shows that the experimental line widths are large and at best of the order of magnitude of 1.5 mT. Thus the extra splittings due to magnetic inequivalency may go undetected. In addition to magnetic inequivalency, other possible reasons for these large experimental line widths in the spectra of  $\text{Ag}_3^{2+}$  are the contribution from overlapping spectra from the silver isotopomers  $^{109}\text{Ag}_3$ ,  $^{109}\text{Ag}_2^{107}\text{Ag}$ ,  $^{109}\text{Ag}^{107}\text{Ag}_2$ , and  $^{107}\text{Ag}_3$  and the coexistence of significant amounts of paramagnetic solvent cations. These cations may cause line broadening via spin-spin interactions and cross-relaxation mechanisms.

Consequently, if isotopically pure Ag species are used and the experiment is designed to minimize the spectral line widths, the extra lines due to magnetic inequivalency may ultimately be detected.

### Conclusions

A tensorial symmetry technique independent of the ground electronic state of a molecule has been used to derive the spin Hamiltonian of  $\text{M}_3$  clusters having  $D_{3h}$  symmetry. The analytical expressions for these tensor components have also been derived using gauge invariant molecular orbital theory. Both methods show that magnetic inequivalency, arising from the application of an external magnetic field, expresses itself naturally in the forms of these spin Hamiltonian tensor components.

The results of this study draw attention to the fact that unless all resonances in an EPR spectrum are resolved and their line shapes simulated to an acceptable degree of accuracy, taking into consideration the effects of magnetic inequivalency, one is not able to unequivocally assign a specific spatial symmetry to a paramagnetic molecule in experiments where an external magnetic field is applied.

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**Registry No.**  $\text{Ag}_3$ , 12595-26-5;  $\text{Ag}_3^+$ , 12595-27-6;  $\text{Ag}_3^{2+}$ , 52227-34-6.

## Kinetics of CO Oxidation over Ru(0001)

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The oxidation of CO over a model Ru(0001) single-crystal catalyst has been studied in a high-pressure reaction-low-pressure surface analysis apparatus. Steady-state catalytic activity as a function of temperature and partial pressure of CO and  $\text{O}_2$  was measured. Both the specific rates and the relative activity ( $\text{Ru} > \text{Pd}$ ,  $\text{Rh}$ ) obtained in this study compare very favorably with the results on high area supported catalysts. Surface concentrations of oxygen were monitored following reaction and found to be dependent on the partial pressures of the reactants. Further, the highest rates of reaction corresponded to reaction on a ruthenium surface covered with a monolayer of oxygen as detected subsequent to reaction by AES. The kinetics measured at various reactant partial pressures (leading to various surface oxygen coverages following reaction) suggest that a chemisorbed atomic oxygen species present at high oxygen coverages may be a crucial reaction intermediate, largely responsible for the optimum reaction rates. Reaction rates under less than optimum conditions ( $\theta_0 < 1$ ) may be limited by different processes and/or involve a different reaction mechanism: notably, the reaction of adsorbed CO with a less active form of chemisorbed oxygen. These results possibly explain the altered relative activity ( $\text{Pd}$ ,  $\text{Rh} > \text{Ru}$ ) observed in ultrahigh vacuum measurements on clean surfaces.

### Introduction

The heterogeneous catalytic oxidation of carbon monoxide has received a great amount of attention owing to the practical and ideal nature of this system. The removal of CO as  $\text{CO}_2$  from automotive exhaust is accomplished in a catalytic converter with the supported noble metals Pt, Pd, and Rh. In this regard, numerous studies of the kinetics as well as investigations into the effects of supports and additives on the kinetics of this reaction over supported catalysts have been reported.<sup>1-8</sup> Additionally, the

relative simplicity of this reaction on a metal surface make it an ideal model system of a heterogeneous catalytic process, a process involving molecular and dissociative (atomic) adsorption, surface reaction, and desorption of products. Thus, the full battery of surface science techniques have had an impact on our understanding of the elementary molecular processes occurring in this reaction.<sup>9-22</sup> Further, the lack of any reported structure sensitivity

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for CO oxidation on the materials studied to date attests to the relevance of the model studies on single crystals.

The recent review by Engel and Ertl<sup>9</sup> discusses in detail the present understanding of the interaction of gaseous CO and O<sub>2</sub> with a metal surface, mutual interactions among the adsorbates, and kinetic measurements of the CO oxidation reaction on well-defined single-crystal surfaces. The connection between these idealized experiments at low pressure and studies on realistic systems at or near atmospheric pressures is also made. There remains, however, at least one anomaly in the comparison between these two sets of experiments. In a survey study,<sup>1</sup> similar activation energies ( $\sim 24$  kcal/mol) and kinetic orders (+1 in O<sub>2</sub> and -1 in CO) were found for supported Pd, Pt, Rh, and Ir catalysts at high pressures with more complex behavior observed for Ru. Further, Ru showed the highest activity for this reaction of the several metals studied.<sup>1</sup> (Despite its high activity, Ru has the unfortunate tendency to form toxic, volatile oxides at the typical temperatures of an automotive catalytic converter making it a poor choice for practical application.) However, in ultrahigh vacuum (UHV) measurements of the kinetics, Ru is clearly the least active of the five metals for this reaction.<sup>9,11,12</sup>

The recent development of the surface science/kinetic hybrid approach for the study of heterogeneous catalysis has led to significant new insights into the nature and concentration of surface species present during catalytic reaction.<sup>23</sup> This approach involves the coupling of a microcatalytic reactor for the measurement of reaction kinetics at realistic pressures with a traditional UHV apparatus for surface analysis. We report here the use of these techniques to study the CO oxidation reaction over a model Ru(0001) single-crystal catalyst. The results provide new information concerning the nature of the surface under high-pressure reaction conditions which can explain the altered relative activity of Ru to other metals in UHV experiments compared to elevated pressure experiments.

### Experimental Section

The studies to be described were carried out utilizing the specialized apparatus discussed in detail in ref 23. This device consists of two distinct regions, a surface analysis chamber and a microcatalytic reactor. The custom-built reactor, contiguous to the surface analysis chamber, employs a retraction bellows that supports the metal single crystal and allows translation of the catalyst in vacuo from the reactor to the surface analysis region. Both regions are of ultrahigh vacuum construction, bakeable, and capable of ultimate pressures of less than  $2 \times 10^{-10}$  Torr. We employ Auger electron spectroscopy (AES) to characterize the sample before and after reaction.

The 1-cm-diameter  $\times$  1-mm-thick Ru single crystal, aligned within  $1/2^\circ$  of the (0001) orientation, was obtained from Metal Crystals and Oxides of Cambridge, England. The crystal was mechanically polished and the orientation double-checked by Laue X-ray backscattering before being spotwelded to two 20-mil W heating leads. A W/5% Re-W/26% Re thermocouple was spotwelded to the edge of the crystal for temperature measurement.

After initially cleaning the Ru crystal with previously published

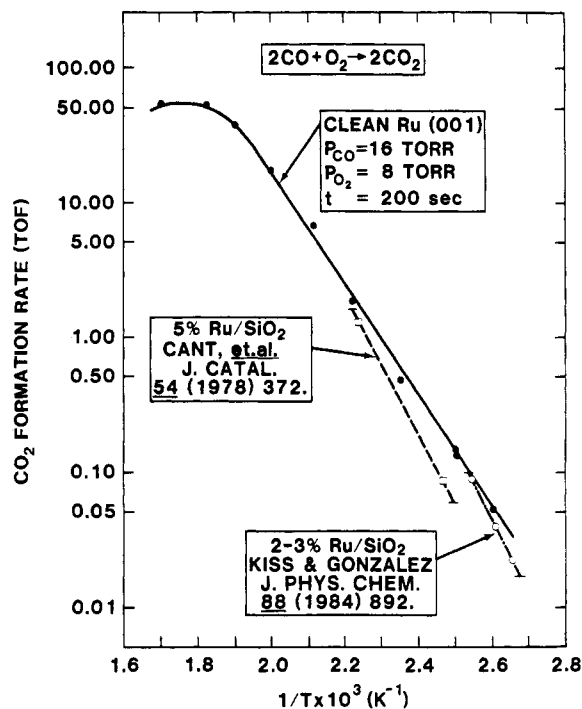


Figure 1. Arrhenius plot of the rate of CO<sub>2</sub> formation (TOF = turnover frequency, number of CO<sub>2</sub> molecules formed per metal surface site per second) over a Ru(0001) catalyst. Also included in the figure are data taken on two silica-supported ruthenium catalysts.<sup>1,2</sup>

procedures,<sup>24</sup> the Auger spectrum was free of O, S, and C contamination. Reactions were then run in the microcatalytic reactor isolated from the main chamber at temperatures from 350 to 625 K with total reactant gas pressures from 9 to 166 Torr. The kinetic data presented throughout this paper were obtained under steady-state reaction conditions (which were reached without any apparent induction time) and at low conversions (typically <5%). CO<sub>2</sub> production was measured by a gas chromatograph equipped with a flame ionization detector (FID). CO and CO<sub>2</sub> were first catalytically converted to methane before detection by the FID. Rates of reaction are expressed as turnover frequencies, TOF (or synonymously as turnover numbers, TON), i.e. CO<sub>2</sub> molecules formed per surface metal atom per second. Surface metal atoms are counted by the measured area of the crystal and the known density of surface atoms on Ru(0001) ( $1.58 \times 10^{15}$  atoms/cm<sup>2</sup>). Following rapid ( $\sim 1$  min) pumpout of the reactant and product gases, the sample is translated back into the surface analysis region for post-reaction characterization. Since CO is known to decompose on Ru when exposed to an electron beam,<sup>25</sup> only surface oxygen could be measured by AES. This analysis was accomplished after flashing the crystal to 600 K to remove adsorbed CO.

O<sub>2</sub> (99.99%) and CO (99.99%) were obtained from Matheson Gas Products. CO was further purified by passing the gas through a glass-wool trap held at liquid nitrogen temperature to remove volatile metal carbonyls. Post-reaction surface analysis as described above indicated the presence of only adsorbed oxygen. In fact, the CO oxidation reaction at stoichiometric reactant gas ratios (CO:O<sub>2</sub> = 2:1,  $P_T = 24$  Torr,  $T = 500$  K,  $t = 200$  s) in the microcatalytic reactor was found to be an extremely efficient method of removing sulfur adsorbed on the surface. An atomically clean surface could then be obtained by flashing the crystal to  $\sim 1550$  K to remove adsorbed oxygen.

### Results

The specific rates of reaction, or turnover frequencies (molecules of CO<sub>2</sub> produced per surface ruthenium site per second), are

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TABLE I

catalyst	$P_{\text{CO}}$ , Torr	$P_{\text{O}_2}$ , Torr	$E_a$ , kcal/mol	$\theta_0$ , ML
2–3% Ru/SiO <sub>2</sub> <sup>a</sup>	26.6	13.2	25.3	
5% Ru/SiO <sub>2</sub> <sup>b</sup>	9.8	4.9	22.5	
Ru(001)	16.0	8.0	19.5	1.0
Ru(001)	16.0	1.0	14.5	0.5
Ru(001)	16.0	0.5	5.7	0.0

<sup>a</sup> Reference 2. <sup>b</sup> Reference 1.

plotted in Arrhenius form in Figure 1. Also included in the figure are data taken on two supported Ru catalysts in two different laboratories.<sup>1,2</sup> The good agreement between the results on the unsupported single crystal and those obtained on the supported catalysts attest to the appropriateness of the model system. Further, it suggests that post-reaction surface characterization of the single crystal will, in many respects, reflect the surface condition of the supported-metal particles. It should be mentioned that studies over the wide temperature (and pressure) range scanned in the experiments reported here are not possible on the supported catalysts due to heat and mass transfer limitations.

As seen in Figure 1, linear Arrhenius behavior is observed below approximately 550 K yielding an activation energy of 19.5 kcal/mol (see Table I). At temperatures above 550 K, the rate rolls over with further increase in temperature, a behavior qualitatively similar to that observed in low-pressure (UHV) measurements of the rate of reaction on Ru(0001).<sup>11,12</sup> In these latter experiments, the maximum rate occurred at a lower temperature (~475 K) than that observed here which may be related to the pressure difference between the two studies (see Discussion section).

The rate of reaction is strongly affected by the CO/O<sub>2</sub> ratio of the gas mixture. This relationship is commonly discussed in terms of the reaction order or partial pressure dependencies of the reactants.<sup>26</sup> A measurement of these reaction orders provides insight into the mechanism and rate-determining elementary steps of the reaction. On supported<sup>1</sup> and single-crystal<sup>27,28</sup> Rh and Pd catalysts, generally first order in O<sub>2</sub> and negative first order in CO dependence is observed for this reaction. (The much more complex behavior observed in UHV studies<sup>9</sup> reflects the ability to vary the surface concentrations of the reactants over a much wider range in these low pressure experiments. This then results in the ability to probe the various steps of the reaction by varying their relative rates.) The order of reaction with respect to CO and O<sub>2</sub> on supported Ru was variable but was significantly different from that observed on Rh and Pd.<sup>1</sup>

We measured the kinetic order for both reactants at 500 K on Ru(0001) by keeping one reactant pressure fixed and varying the other. The results are shown in Figures 2A and 3A. At low oxygen partial pressures (Figure 2A), the reaction is positive order in O<sub>2</sub>. The slope of the curve changes for O<sub>2</sub> pressures above about 4 Torr becoming zero order in O<sub>2</sub>; that is, further increase in O<sub>2</sub> pressure has no effect on the rate of reaction. The dependance of the rate on CO partial pressure (Figure 3A) is somewhat more complex. At low CO partial pressures, the dependance is approximately positive first order in CO. This changes to negative first-order dependance at CO partial pressures above about 16 Torr.

Surface concentrations of oxygen following reaction were monitored by AES and also found to be dependant on the partial pressures of the reactants. This dependance is illustrated in Figures 2B and 3B for varying O<sub>2</sub> and CO partial pressures, respectively. The post-reaction surface oxygen level rises from zero at low O<sub>2</sub> partial pressures to a constant value at O<sub>2</sub> pressures exceeding about 8 Torr (Figure 2B). Approximate reciprocal behavior is observed as a function of CO partial pressure (Figure 3B). Here,

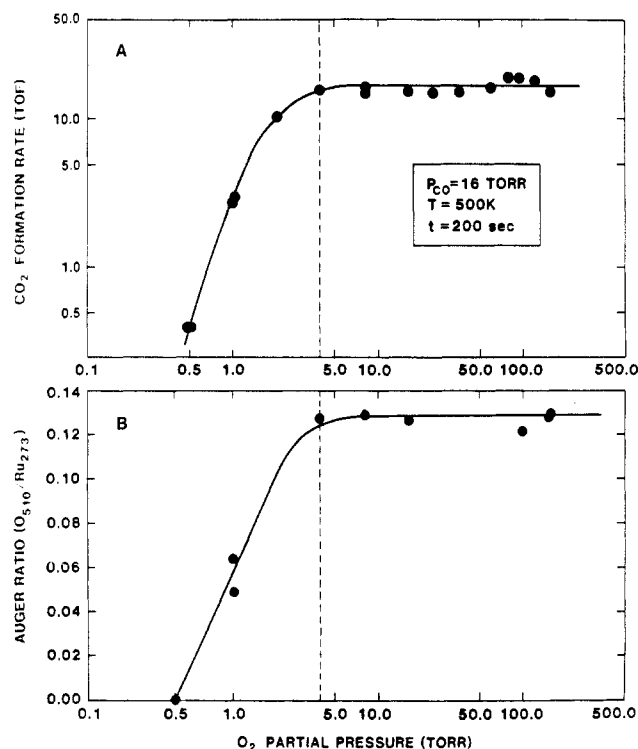


Figure 2. A comparison of the effect of O<sub>2</sub> partial pressure on the rate of reaction and the level of surface oxygen detected following reaction by AES. The Auger ratio, O<sub>510</sub>/Ru<sub>273</sub>, is the ratio of the peak-to-peak heights of the oxygen KLL transition at 510 eV to the ruthenium MNN transition at 273 eV.

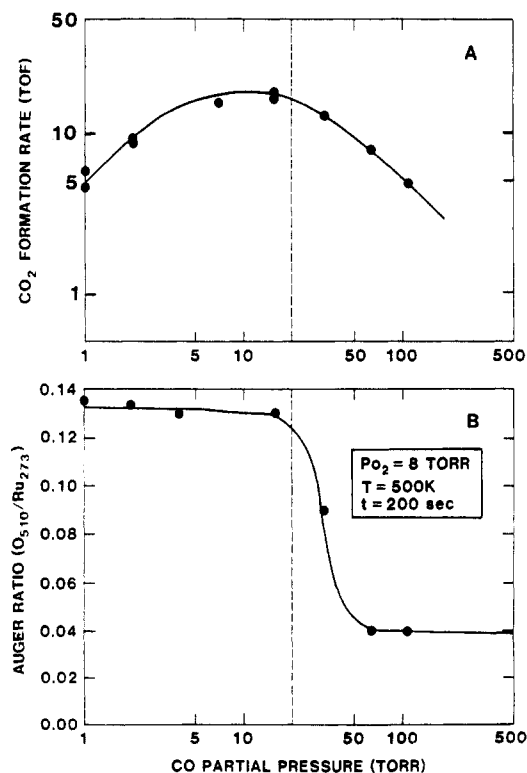


Figure 3. A comparison of the effect of CO partial pressure on the rate of reaction and the level of surface oxygen following reaction.

the surface oxygen level is constant at low CO partial pressures, falling at pressures above about 16 Torr to a level approximately 1/4 of that observed at low CO pressures.

The dashed vertical lines are drawn in Figures 2 and 3 to emphasize the correlation between the post-reaction surface oxygen level and the rate of reaction. In fact, the dependance of the rate of reaction and the level of surface oxygen on the partial pressures

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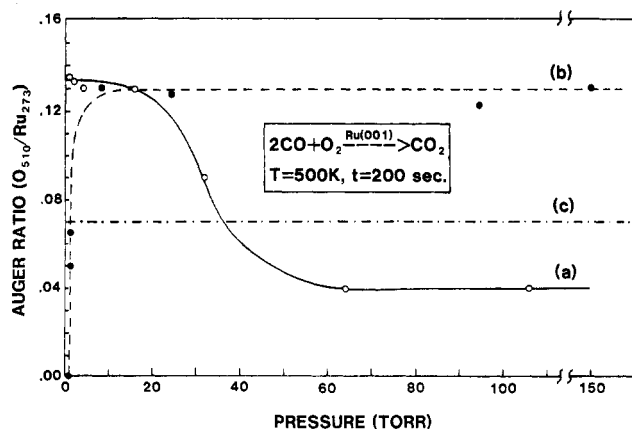


Figure 4. The effect of changes in the partial pressures of the reactants on the level of surface oxygen present following reaction: (a)  $P_{O_2} = 8$  Torr,  $P_{CO} = x$ ; (b)  $P_{CO} = 16$  Torr,  $P_{O_2} = x$ ; (c) the level of surface oxygen present following a 20-langmuir dose of  $O_2$  in UHV.

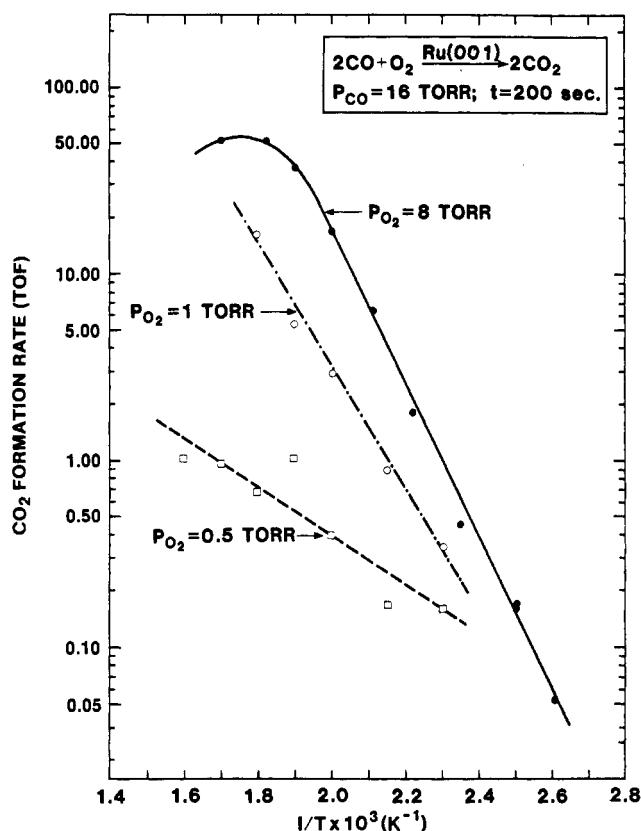


Figure 5. Arrhenius plot of the rate of CO oxidation over a Ru(0001) catalyst at various  $O_2$  partial pressures.

of oxygen (Figure 2) are virtually identical. In Figure 3, both the reaction rate and the oxygen level fall for CO partial pressures above 16 Torr. Note that optimum rates of CO oxidation occur on a ruthenium surface with the largest amount of surface oxygen remaining after reaction. Further, this saturation amount of oxygen is approximately twice the level obtained by a low-pressure (20 langmuir) exposure of  $O_2$  in UHV as determined by AES (Figure 4) and TPD.

Not only are the reaction rates and surface oxygen levels falling as the  $O_2$  partial pressure is lowered below 4 Torr (Figure 2), but, as seen in Figure 5, the apparent activation energy is also affected. The Arrhenius data shown in the figure were taken at CO partial pressures of 16 Torr and  $O_2$  partial pressures of 8.0, 1.0, and 0.5 Torr. Reaction under these conditions resulted in relative post-reaction levels of oxygen of 1.0, 0.5, and 0.0, respectively (Figure 2), and the activation energies measured are presented in Table I.

In order to more fully assess the relevance of this surface oxygen,

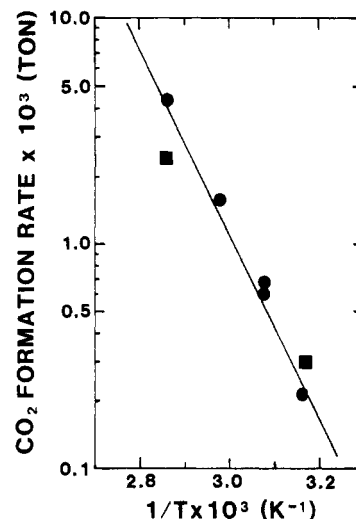


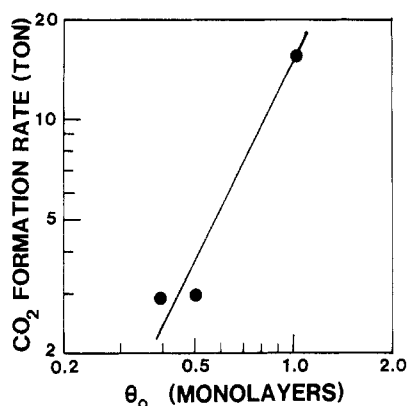
Figure 6. Rate of oxygen atom removal by high pressures of CO ( $\blacksquare$ ,  $P_{CO} = 16$  Torr;  $\bullet$ ,  $P_{CO} = 8$  Torr). The surface was precovered with a monolayer of oxygen and the reaction followed by AES. The solid line is an extrapolation of the rate of  $CO_2$  formation under optimum reaction conditions (see text) from Figure 1.

we performed separate titration experiments in which the surface was precovered with a monolayer of oxygen by running a CO oxidation reaction in the high-pressure reactor ( $P_{CO} = 8$  Torr,  $P_{O_2} = 8$  Torr,  $T = 500$  K,  $t = 200$  s). This sample was then exposed to high pressures of CO at various temperatures. The CO pressures used in these experiments (8 and 16 Torr) were chosen to coincide with conditions where steady-state reaction was zero order in CO pressure and optimum reaction rates were observed (Figure 3). The drop in oxygen coverage ( $\Delta\theta_0$ ) with time was followed by AES and the turnover numbers for  $CO_2$  production were based on the AES estimates of relative coverage assuming that one  $CO_2$  molecule was formed for each oxygen atom removed from the surface (saturation,  $\theta_0(\max)$ ,<sup>29</sup> was assumed to be 1 monolayer (ML),  $1.58 \times 10^{15}$  O atoms/cm<sup>2</sup>; see Discussion). The specific rates for the limiting case of  $\theta_0 \sim 1$  ML and small  $\Delta\theta_0$  are shown in Figure 6. The solid line in the figure represents an extrapolation of the Arrhenius curve obtained under optimum reaction conditions ( $\theta_0 = 1$ ) from Figure 1. The initial rates of  $CO_2$  formation obtained in the titration experiments (shown in Figure 6) were always greater than the rates obtained at later times (larger  $\Delta\theta_0$ ) and those obtained when the initial  $\theta_0$  was significantly less than 1 ML.

## Discussion

Of critical importance to the study of catalysis by model experiments with unsupported single crystals is to initially determine the relevance of the model systems. The CO oxidation reaction has been reported to be structure insensitive, or facile.<sup>9,27</sup> For other facile reactions such as CO and ethylene hydrogenations, excellent agreement between the kinetics measured on real-world supported catalysts and studies on different crystal faces of model single-crystal catalysts has been demonstrated.<sup>23</sup> A comparison of the measured kinetics of the CO oxidation reaction on the model Ru(0001) and on silica-supported Ru catalysts as shown in Figure 1 again shows remarkably good agreement. Further, we find that the activity measured on the ruthenium single crystal is significantly greater than that obtained for Rh(111)<sup>27</sup> and Pd(110)<sup>28</sup> surfaces, again in agreement with the relative activities of supported metal catalysts.<sup>1</sup> As discussed earlier, in low-pressure UHV experiments, it was determined that Ru was the least active metal

(29) We use this notation,  $\theta_0(\max)$ , to avoid confusion with the saturation coverage obtainable with moderate ( $<100$  langmuirs) exposures in UHV,  $\theta_0(\text{sat})$ , and the coverage at which an optimum ( $2 \times 2$ ) LEED pattern is obtained, defined by Madey et al.<sup>13</sup> as  $\theta_0(\text{opt})$ . Madey<sup>13</sup> has shown that  $\theta_0(\text{sat}) = 2\theta_0(\text{opt})$ . We show (see text) that  $\theta_0(\max) = 2\theta_0(\text{sat})$ . Parrott et al.<sup>18</sup> were able to obtain an oxygen coverage of 1 ML ( $\theta_0(\max)$ ) by exposing a Ru(0001) crystal to 6000 langmuirs at 300 K. This sample gave the expected ( $1 \times 1$ ) LEED pattern.



**Figure 7.**  $\text{CO}_2$  formation rate as a function of surface oxygen coverage. The data point at 1 ML is an average of several points.

studied in contrast to the high-pressure results. We now explore a possible explanation for this discrepancy.

The presence of a chemisorbed surface oxygen species was noted from the AES surface analysis following steady-state reaction. In addition, the changes in the level of this surface oxygen with changing oxygen pressures were correlated with changes in the rate of reaction. As seen in Figures 2 and 3, an optimum rate of CO oxidation corresponds to reaction on a ruthenium surface with the largest amount of surface oxygen ( $\theta_O(\text{max})$ ) remaining after reaction. These results contrast significantly with the behavior of Rh(111)<sup>27</sup> and Pd(110)<sup>28</sup> surfaces under similar conditions in which case no surface oxygen is detected by AES following steady-state reaction. The reaction on Rh(111) was seen to deactivate when  $\text{O}_2/\text{CO}$  ratios exceeded  $\sim 30:1$ . At this time, a surface oxygen species was present on the surface and the rate became negative order in  $\text{O}_2$  pressures.<sup>22,27</sup> Clearly, the presence of this surface "oxide" on Rh(111) is responsible for the deactivation of the catalyst.

It is possible to quantify the maximum coverage of oxygen on Ru(0001) ( $\theta_O(\text{max})$ ) obtained after reaction at optimum rates. As shown in Figure 4, this surface coverage is, within experimental error, exactly twice the level obtained by a low pressure (20 langmuirs) exposure of  $\text{O}_2$  in UHV, i.e.  $\theta_O(\text{max}) = 2\theta_O(\text{sat})$ .<sup>29</sup> Although  $\theta_O(\text{sat})$  was initially thought to be equal to 1,<sup>13</sup> more recent studies have concluded that  $\theta_O(\text{sat}) = 1/2$ ;<sup>18</sup> that is, exposure of Ru(0001) to less than 100 langmuirs of  $\text{O}_2$  in UHV leads to a surface O/Ru ratio of 1/2. This then indicates that under optimum high-pressure reaction conditions, the ruthenium surface is completely covered by oxygen to a stoichiometric ratio of 1. We have also measured these coverages by  $\text{O}_2$  thermal programmed desorption. Integration of the TPD peak areas indicated that  $\theta_O(\text{max}) \sim 2\theta_O(\text{sat})$ , in agreement with the AES results. It should be mentioned that this quantitative analysis may well be complicated by the apparent tendency of atomic oxygen to penetrate into the first few layers below the surface of Ru(0001) at temperatures as low as 400 K.<sup>19</sup> These authors have also noted that the amount of  $\text{O}_2$  desorbed from precovered Ru(0001) may not be equal to the amount adsorbed (see Figure 3 of ref 19). What is clear, however, is that reaction on atomically clean Ru in UHV experiments does not duplicate the surface condition of a ruthenium catalyst under realistic pressure conditions. This probably accounts for the altered relative activity of Ru to other metals in the UHV studies compared to the elevated pressure experiments.

The presence of additional surface oxygen subsequent to high-pressure reaction suggests that the additional oxygen may be a crucial reaction intermediate and largely responsible for the kinetics of reaction over Ru under optimum conditions. Consistent with this conclusion, the rate of the titration reaction at high coverages ( $\theta_O(\text{max})$ ) of adsorbed oxygen with CO is identical with the overall reaction rate (Figure 6). Further, the titration reaction rate is considerably reduced at lower oxygen coverages. These results not only indicate that the adsorbed oxygen present at high coverages is one of the reaction intermediates, but also that the reactivity of adsorbed oxygen increases with coverage. This latter

conclusion is supported by the dependence of the overall reaction rate with oxygen coverage at a fixed CO pressure, data contained in Figure 2, A and B, and shown in Figure 7. Here it can be seen that the rate is proportional to  $\theta_O^{2.1}$ . A single reactive form of adsorbed oxygen would be expected to give a linear dependence of the rate on oxygen coverage.<sup>27a</sup> Similar results have been obtained recently on Ag(110)<sup>21</sup> where additional oxygen deposited by a 50-Torr  $\text{O}_2$  exposure was found to be much more reactive with CO compared with surface oxygen at levels obtained in UHV exposures. Also, note that not only is the reaction rate attenuated at low  $\text{O}_2$  partial pressures (Figure 2), but the activation energy is also profoundly affected (Figure 5 and Table I). The change in the activation energy under conditions when significantly less than maximum coverages of oxygen are present on the surface implies a change in the reaction mechanism or possibly a change in the rate-determining step of the reaction. Reaction of CO with a less active form of surface oxygen (or vice versa) should involve a process with very different kinetics (prefactors and activation energies).

In contrast to the results reported here, Kiss and Gonzalez<sup>2</sup> report rapid deactivation of a Ru/SiO<sub>2</sub> catalyst in oxygen-rich gas mixtures at  $\text{CO}/\text{O}_2$  ratios  $\leq 1$ . They attributed this result to the formation of a tightly bound subsurface oxygen species which reacted much more slowly with CO. Under similar pressure conditions, we observe virtually no deactivation of the Ru(0001) single crystal for  $\text{CO}/\text{O}_2$  ratios as low as 0.1. White and co-workers<sup>19</sup> have obtained evidence for a subsurface oxygen species on Ru(0001) at temperatures as low as 400 K, although there is no indication that such species form under our reaction conditions. The possibility remains, however, that oxygen may enter the subsurface region more rapidly at imperfections such as steps or kinks than on the flat terraces of low Miller index planes. The greater abundance of such defects on small particles could therefore play a role in the rate of bulk oxidation under these conditions.

An analysis of the pressure dependence of the rate of reaction can provide insight into the possible rate-determining elementary processes occurring on the surface. For example, at low temperatures when CO coverages on the surface are appreciable, the rate of reaction on many supported catalysts was found to be approximately proportional to  $\text{O}_2$  and inversely proportional to CO partial pressures. This behavior is taken as a reflection of the ability of CO to better compete for available adsorption sites on the surface at low temperatures. Consistent with this is the approximate similarity between the activation energy measured for the reaction and that for desorption of CO. However, extrapolation of this simple analysis to other experimental conditions is complicated by the possibility for differing activities of various forms of oxygen on the surface. Just such reactivity differences have been demonstrated by, for example, Campbell and Paffett<sup>21</sup> and Stuve et al.<sup>20</sup> Further, these latter authors provide evidence for a low-temperature reaction of a CO-Pd-O complex, i.e. different forms of active CO.

The experiments reported here on model single-crystal Ru(0001) have afforded the opportunity to probe a much wider temperature and pressure range than is possible on supported catalysts. The added dimension of post-reaction AES surface analysis has provided key information necessary for a complete discussion of the reaction mechanism or mechanisms under the various experimental conditions. Let us first discuss the pressure dependence of the reaction when the surface is covered to a maximum with oxygen ( $\theta_O = \theta_O(\text{max})$ ). As seen from Figures 2 and 3, under optimum conditions, the reaction is zero order in both CO and  $\text{O}_2$  partial pressures. Further, the rate (prefactor and activation energy) to titrate surface oxygen from a fully covered oxygen surface is identical with the steady-state reaction rate on such a surface. This behavior indicates that the overall rate is being controlled by the surface reaction (Langmuir-Hinshelwood) step. The energetics measured under these conditions ( $E_a = 19.5$  kcal/mol) should then represent the activation energy for this step of the reaction. At low CO partial pressures ( $< 8$  Torr), the reaction is approximately first order in CO pressure (Figure 3A). Under these conditions, the reaction is now limited by the adsorption of

CO onto the surface. If we assume that the change of the rate from first order to zero order in CO pressure occurring at 8 Torr represents the saturation of CO adsorption on this highly oxygen-covered surface at the reaction temperature of 500 K, and that CO adsorption remains nonactivated on this surface, a CO binding strength of approximately 18.5 kcal/mol can be calculated.<sup>30</sup> This value is significantly less than that observed for CO on clean Ru(0001) where values ranging from 23 to 28 kcal/mol have been measured.<sup>31</sup>

A reduction of the CO bonding strength on the oxygen-covered Ru surface from that obtained on clean Ru may also explain the nonlinear Arrhenius behavior observed at stoichiometric reactant gas ratios (CO:O<sub>2</sub> = 2:1) and temperatures above about 525 K (Figure 5). Such a falloff in activity is not observed at reduced oxygen pressures (i.e., low  $\theta_O$ ) for temperatures as high as 625 K. The reduced CO bonding strength on the fully oxygen-covered Ru surface could lead to a departure of the CO coverage from saturation at temperatures above 525 K. This fall in CO coverage from saturation would then lead to the observed nonlinear Arrhenius behavior. In support of this, the above estimate of 18.5 kcal/mol as the binding strength for CO on an oxygen-saturated surface suggests<sup>30</sup> that, for a CO partial pressure of 16 Torr, the coverage of CO will depart significantly from unity at approximately 550 K.

At lower oxygen coverages ( $\theta_O < \theta_O(\max)$ ), Figures 2 and 3 show that the reaction is now positive order in O<sub>2</sub> and approximately negative first order in CO pressure. The positive order in O<sub>2</sub> is an indication that the reaction rate is now limited by oxygen adsorption. The negative order in CO indicates site blocking of O<sub>2</sub> chemisorption by adsorbed CO. The energetics measured under these conditions (i.e., low  $\theta_O$ ) suggest a modification of either the rate-determining step or the overall reaction mechanism.

In discussing these pressure dependancies, it is important to note the possible heterogeneous nature of the adsorbed layer. On Pd(111) in UHV experiments, high coverages of coadsorbed O and CO lead to islands of pure adsorbates as well as domains in which O and CO are uniformly mixed.<sup>9</sup> It would be highly instructive to investigate the structure and composition of the

adsorbed overlayer after reaction at elevated pressures. Further, an independent measurement of the binding strength of CO on an oxygen-saturated surface, estimated earlier to be 18.5 kcal/mol, is desirable. A recent report of experiments utilizing LEED, AES, XPS, and thermal desorption to probe the nature of a Ag(110) surface following catalytic ethylene epoxidation<sup>32</sup> demonstrates the importance of such studies.

### Summary

Model kinetic studies of the CO oxidation reaction on a single-crystal Ru(0001) catalyst as a function of reactant partial pressures and temperature have demonstrated the following:

1. Specific rates of reaction (turnover numbers) measured on the single crystal (site density derived from the Ru atom density on the (0001) plane) are in excellent agreement with those obtained on high area supported catalysts (site density derived from chemisorption data).

2. The relative order of activity (Ru > Pd, Rh) observed on supported catalysts is also reproduced by the model single crystal. This agreement attests to the appropriateness of the model system and the relevancy of the post-reaction surface analysis carried out in the study reported here.

3. Reaction under optimum conditions is correlated with the presence of a monolayer of oxygen on the Ru surface as detected by AES subsequent to steady-state reaction. Kinetics measured under conditions when less oxygen is detected after reaction differ significantly suggesting the importance of a chemisorbed oxygen intermediate. These results possibly explain the altered relative activity (Pd, Rh > Ru) observed in UHV measurements on clean surfaces.

4. Reaction rates under nonoptimum conditions ( $\theta_O < 1$ ) may be limited by different processes and/or involve a different reaction mechanism; notably, the reaction of adsorbed CO with a less active form of chemisorbed oxygen atoms.

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## Electrochemical Growth of Metal Interlayers in Polyimide Film

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Films of polyimide coated on the surface of an electrode can accept electrons while cations from solution permeate from the opposite surface. When the electrolyte solution includes salts of metals (Ag<sup>+</sup>, Cu<sup>+</sup>, and Au<sup>+</sup>) whose reduction potentials are positive of that for the polymer, the zerovalent metals may be deposited as a thin electrically conductive and optically reflective layer embedded within the polymer, an "interlayer". The morphology of these interlayers can be explained on the basis of a transport-limited process which can function in steady state. A simple diffusion model for the steady-state transport conditions gives a good quantitative account for the dependence of interlayer position upon applied potential and metal ion concentration. More complex interlayer morphologies may be developed by altering the experimental variables during the course of the process. Two-dimensional patterns have been produced by limiting the supply of either electrons or ions to specified regions of the film's surface.

### Introduction

Polyimides derived from aromatic dicarboxylic anhydrides constitute an increasingly important class of commercial polymers.<sup>1</sup>

Structure I (Scheme I) derived from pyromellitic dianhydride and 4,4'-oxydianiline is perhaps the most familiar representative and is especially valued for its high-temperature stability and excellent

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