Catalysis Letters 9 (1991) 65–70

THE MECHANISM OF CO OXIDATION OVER Cu(110): EFFECT OF CO GAS ENERGY.

Melanie E. DOMAGALA and Charles T. CAMPBELL *

Department of Chemistry, University of Washington, Seattle, Washington 98195, U.S.A.

Received 10 January 1991; accepted 11 March 1991

The effect of the temperature of gas phase CO upon the kinetics of the oxygen titration reaction: $CO_g + O_a \rightarrow CO_{2,g}$, has been studied. It is found that the reaction's rate is independant of CO gas temperature between 300 and 623 K. The activation energy (6.5 kcal/mole), dependence upon CO pressure (first-order), and independence upon oxygen coverage for $0.1 \leq \theta_O \leq 0.4$ are all independant of the CO gas phase temperature. This result rules out any Eley-Rideal type mechanism whereby CO reacts directly from the gas phase with an oxygen adatom without first being accommodated to the surface temperature in an absorbed state. The result is instead interpretable in terms of a Langmuir-Hinshelwood mechanism.

Keywords: CO oxidation on Cu(110), Langmuir-Hinshelwood mechanism

1. Introduction

The reaction between CO and absorbed oxygen atoms (O_a) on copper surfaces is of interest because of the important role it plays in many catalytic reactions. Specifically, it is thought that CO and CO_2 actively interconvert via an O_a intermediate during both the water-gas shift ($H_2O + CO \rightarrow H_2 + CO_2$) and methanol synthesis reactions ($CO + 2H_2 \rightarrow CH_3OH$) over Cu and Cu/ZnO catalysts [1,2].

The titration reaction $CO + O_a \rightarrow CO_2$ on Cu (110) has been studied extensively by several groups. Habraken and coworkers [3,4] and van Pruissen and coworkers [5,6] have studied the interaction of CO gas with oxygen covered Cu(110) in the temperature range 475 to 775 K. They observed a first order dependence of the rate (R) upon the partial pressure of CO (P_{CO}) and measured an apparent activation energy (E_{app}) of 6.3 to 7.1 kcal/mole for oxygen coverages (θ_O) between 0.1 and 0.4. These results have most recently been interpreted in

---

* Camille and Henry Dreyfus Foundation Teacher-Scholar Fellowship.

terms of a Langmuir-Hinshelwood (LH) mechanism which consists of the following elementary steps [5]:

$$CO_g \Leftrightarrow CO_a \tag{1}$$

$$CO_a + O_a \rightarrow CO_{2,g}. \tag{2}$$

They assumed that the CO coverage was low and that the step $CO_g \Leftrightarrow CO_a$ was in rapid equilibrium, and therefore the overall rate could be written as follows:

$$R_{LH} = v_{LH} v_A / v_D \exp - (E_{LH} + \Delta H_{ad})/RT \, P_{CO} \theta_O, \tag{3}$$

where E_{LH} is the activation energy for the Langmuir-Hinshelwood step (2), ΔH_{ad} is the adsorption enthalpy associated with step (1), and the preexponential factors (v_i) refer to the Langmuir-Hinshelwood step (v_{LH}), desorption of CO (v_D), and adsorption of CO (v_A). The value v_A takes into consideration the effect of oxygen coverage upon the sticking probability for CO which was assumed to be proportional to the factor ($\theta_{max} - \theta_O$), where θ_{max} is an adjustable parameter. With an appropriate value for θ_{max} [5], this dependence in eq. (3) reproduces well the experimental result that the rate of titration was nearly independant of θ_O between 0.1 and 0.4 [5]. This model also appropriately reproduces the observed first-order dependence of the rate upon P_{CO}. According to this model, the apparent activation energy is then simply given by:

$$E_{app} = E_{LH} + \Delta H_{ad}. \tag{4}$$

Since ΔH_{ad} is about $-(12-13)$ kcal/mole on Cu(110) [2,7], the observed value of 6.3–7.1 kcal/mole for E_{app} implies an activation energy of ~ 18–20 kcal/mole for the elementary LH reaction step.

It should be recognized, however, that the previously observed kinetics could just as easily have been explained within an Eley-Rideal (ER) mechanism, whereby a CO gas molecule reacts directly with an oxygen adatom in the elementary reaction step without first being accommodated to the surface temperature:

$$CO_g + O_a \rightarrow CO_{2,g}. \tag{5}$$

According to this mechanism, the reaction rate would be expressed as:

$$R_{ER} = v_{ER} \exp(-E_{ER}/RT) P_{CO} \theta_O, \tag{6}$$

where E_{ER} is the activation energy for step (5). Again, if v_{ER} is allowed to vary appropriately with θ_O (due to lateral interactions in the adlayer or steric effects), this expression could adequately reproduce the observed near independence of the rate on θ_O for $0.1 \leq \theta_O \leq 0.4$ and the first-order dependence on P_{CO}. According to this mechanism, the apparent activation energy of ~ 7 kcal/mole directly gives the value of E_{ER} for step (5).

We present here, however, direct evidence that the rate of this titration reaction does not depend upon the temperature of CO_g but only upon the surface temperature, which was independently varied over the range 300–623 K. This result is inconsistent with an elementary reaction step of the type $CO_g + O_a \rightarrow CO_{2,g}$ since that step must also have an activation energy of ~ 7 kcal/mole. This result helps strengthen the evidence that this titration reaction occurs via the Langmuir-Hinshelwood mechanism, only assumed previously on Cu(110). Although this mechanism was previously proven on other transition metals (i.e. Pt [8] and Pd [9]), it was not obvious that it should also occur on Cu since Cu surfaces bind CO_a much more weakly, and since this reaction's probability per CO collision with the surface is some four orders-of-magnitude lower on Cu than on Pt or Pd.

2. Experimental

The ultrahigh vacuum (UHV) apparatus and attached microreactor for this experiment has been described elsewhere [10,12]. The carbon monoxide (99.99%) and oxygen (research grade) used were purchased from Airco. Gas purity was checked in vacuo by mass spectrometry. The Cu(110) crystal was cleaned by Ar^+ ion sputtering at 470 K followed by annealing at 830 K. Surface cleanliness was checked by AES, LEED, and thermal desorption. The crystal was then dosed with a near saturation coverage of O_2(~ 11 L at 300 K, to give $\theta_O \sim 0.45$). Absolute coverages are reported relative to the Cu(110) surface atom density where $\theta = 1$ corresponds to 1.085×10^{15} cm^{-2} on Cu (110). Absolute oxygen coverages were measured by the O(510 eV)/Cu(930 eV) AES ratio. A ratio of 0.085 was assigned previously to a coverage of $\theta = 0.5$ [11]. This coverage gave a work function change relative to clean Cu ($\Delta\phi$) of approximately +330 meV, which is consistent with previous observations [4]. The oxygen-covered crystal was then heated to the reaction surface temperature, T_s, and finally translated into an attached microreactor which contained CO_g and $N_{2,g}$ at controlled partial pressures ($P_{CO} = 10^{-4}$ to 10^{-3} Torr, $P_{N2} = 0$ to 50 Torr). This slow-flow type reactor was designed so that the partial pressures of CO and N_2 did not change due to reaction, and so that these pressures could be measured by mass spectrometry as described elsewhere [12]. Periodically this exposure to CO_g was interrupted by translating the sample back into UHV for a $\Delta\phi$ measurement. (Our non-destructive method of measuring $\Delta\phi$ is described in [12].) Since below $\theta_O = 0.5$ the value of $\Delta\phi$ is known to be proportional to θ_O [4], this $\Delta\phi$ was then easily used as a rapid measure of θ_O. (At these T_S and P_{CO}, the coverage of CO_a is too low to measurably alter $\Delta\phi$ [13].) A slope of θ_O (via $\Delta\phi$) verses exposure time to CO_g was used to determine the rate ($d\theta_O/dt$) of the net titration reaction $CO_g + O_a \rightarrow CO_{2,g}$ as a function of θ_O.

This type of titration was then repeated at different surface temperatures, CO partial pressures, and N_2 partial pressures. As described previously in our study of the net reaction $H_{2,g} + O_a \rightarrow H_2O_g$ [12], the addition of N_2 from 0 to 50 Torr has the effect of raising the temperature (T_g) of the CO_g molecules which collide with the Cu surface from the temperature of the reactor walls (300 K) to the temperature of the sample surface (448 to 623 K). This occurs because the gas mean-free-path is much larger than the distance from the surface to the walls (~ 2 cm) in the absence of N_2, but less than 10^{-4} of this distance at 50 Torr of N_2. In this way, we were able to independently determine the effects of T_S, T_g, P_{CO}, and θ_O upon the rate of oxygen removal by CO.

3. Results

In the absence of N_2, our kinetic results are quite similar to those found in previous studies [3–6]:

1. The reaction rate was first-order in P_{CO} in the range 10^{-3} to 10^{-4} Torr for $0.1 \leq \theta_O \leq 0.4$.
2. The rate at constant P_{CO} demonstrated an apparent activation energy of 6.5 ± 0.2 kcal/mole in the surface temperature range 448 to 623 K for $0.1 \leq \theta_O \leq 0.4$. (Note that only T_S was varied, here but not T_g.)
3. The rate was nearly independant of θ_O in the coverage range $0.1 \leq \theta_O \leq 0.4$, but decreased with θ_O for $\theta_O < 0.05$.
4. The reaction probability (rate per CO collision with the surface) was 2.5×10^{-5} at a surface temperature of 623 K and $0.1 \leq \theta_O \leq 0.4$.

None of these results changed within experimental error when 50 Torr of N_2 was added to the reaction vessel. (The slight change in CO collision frequency with the surface due to its change in temperature was considered in calculating the reaction probability here.) This result proves that the reaction rate was independant of the gas phase temperature of the CO_g hitting the surface for the range $T_g = 300$ to 623 K.

4. Discussion

The kinetics we have observed are indeed consistent with the LH mechanism proposed previously [5], but not consistent with an ER mechanism. Most notable is our only truly new result, which is that the rate is independent of the CO gas temperature between 300 and 623 K. According to the ER mechanism, gas phase CO would be directly involved in the elementary step which has a 6.5 kcal/mole activation energy (see Introduction). Depending upon where this barrier occurred along the reaction coordinate, all or only part of it might be accessible with the gas-phase CO degrees of freedom. However, even if only 15% of it were accessible, via the energy of CO_g, one would expect a 150% increase in the reaction rate as T_g is increased from 300 K to 623 K. This is outside the error bars of our measurements, which strongly suggests that a direct impact type of ER mechanism is not an appropriate description of the reaction event.

On the other hand, the independence of the reaction rate upon T_g is easily understandable within the LH mechanism proposed previously (see Introduction). The only elementary step involving CO_g directly in this mechanism is the sticking or adsorption reaction: $CO_g \rightarrow CO_a$. Since that step is known to occur with nearly unit sticking probability even at the low temperatures where it has been measured (100–200 K) [7], it is unlikely to have any significant activation barrior. That is, the sticking probability can not increase any further on going to $T_g = 300$ or 623 K. If anything, the sticking probability may decrease slightly between 300 and 623 K due to dynamical effects associated with collisional energy loss [14]. This effect is expected to be small ($< 50\%$) [14,15] and probably below the error bars associated with our measurement of reaction probability. (These error bars are a factor of ~ 1.7 at 95% confidence limits, due mostly to the difficulty of accurately measuring P_{CO} in the presence of 50 Torr N_2).

In conclusion, it appears that the net reaction $CO_g + O_a \rightarrow CO_{2,g}$ occurs via a CO_a intermediate on Cu(110), just as has been proven on Pd [9] and Pt [8] surfaces. Thus, the much weaker metal-CO bond in the case of Cu does not result in a fundamentally different mechanism for this reaction. The fact that this reaction's probability per CO collision with the surface is some four orders-of-magnitude lower on Cu than on Pt or Pd is, however, related to this weaker CO adsorption energy on Cu since it results in a much higher desorption rate for CO_a. This higher desorption rate means that a CO_a will desorb with a much higher probability than it's probability for reacting with an O_a, whereas on Pt and Pd surfaces, the reverse is true [8,9].

As a point of proof, we have recently shown, using the same experimental methods, that an increase in T_g from 300 K to 623 K results in a ~ 30-fold increase in the rate of the net reaction: $H_{2,g} + O_a \rightarrow H_2O_g$. In that case, the change in rate is due to a 14 kcal/mole activation energy for the step $H_{2,g} \rightarrow 2H_a$, largely accessible via the $H_{2,g}$ translational degrees of freedom [12].

Acknowledgements

The authors would like to acknowledge technical assistance from Joseph M. Campbell and financial support for this research from the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division.

References

[1] D.S. Newsome, Catal. Rev.-Sci. Eng. 21 (1980) 275.
[2] J. Nakamura, J.M. Campbell and C.T. Campbell, J. Chem. Soc., Faraday Trans. 86 (15) (1990) 2725.

[3] F.H.P.M. Habraken and G.A. Bootsma, Surface Sci. 87 (1979) 333.

[4] F.H.P.M. Habraken and G.A. Bootsma, P. Hoffmann, S. Hachicha and A.M. Bradshaw, Surface Sci. 88 (1979) 285.

[5] O.P. van Pruissen, M.M.M. Dings and O.L.J. Gijzeman, Surface Sci. 179 (1987) 377.

[6] O.P. van Pruissen, O.L.J. Gijzeman and J.W. Geus, Vacuum 38 (4/5) (1988) 247.

[7] (a) K. Horn, M. Hussain and J. Pritchard, Surface Sci. 63 (1977) 244;
(b) J.A. Rodriguez, J. Phys. Chem. 93 (1989) 5258.
(c) C. Harendt, J. Goschnick and W. Hirshwald, Surface Sci. 152 (1985) 453.

[8] (a) T.W. Engel, J. Chem Phys. 69 (1978) 373.
(b) T. Engel and G. Ertl, J. Chem. Phys. 69 (1978) 1267.

[9] C.T. Campbell, G. Ertl, H. Kuipers and J. Segner, J. Chem. Phys. 73 (1980) 5862.

[10] W.D. Clendening and C.T. Campbell, J. Chem Phys. 90 (1989) 6656.

[11] W.D. Clendening, J.A. Rodriguez, J.M. Campbell and C.T. Campbell, Surface Sci. 216 (1989) 429.

[12] (a) J.M. Campbell, M.E. Domagala and C.T. Campbell, J. Vac. Sci. Technol. (in press);
(b) J.M. Campbell and C.T. Campbell (in preparation).

[13] This can be calculated using the formula for the equilibrium θ_{CO} (eq 1) given in ref. [2].

[14] (a) W.H. Weinberg and R.P. Merrill, J. Vac. Sci. Technol. 8 (1981) 718;
(b) C.T. Rettner, C.B. Mullins, D.S. Bethune, D.J. Auerbach, E.K. Schweizer, W.H. Weinberg, J. Vac. Sci. Technol. A8 (1990) 2699.

[15] (a) C.T. Campbell, G. Ertl, H. Kuipers and J. Segner, Surface Sci. 107 (1981) 207;
(b) J. Segner, C.T. Campbell, G. Doyen and G. Ertl, Surface Sci. 138 (1984) 505.