

## SURFACE RESIDENCE TIMES AND REACTION MECHANISM IN THE CATALYTIC OXIDATION OF CO ON Pd(111)

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Using the modulated molecular beam technique it has been possible to uniquely determine the reaction mechanism for the catalytic oxidation of CO on a Pd(111) surface through the determination of surface residence times. The reaction takes place between chemisorbed CO molecules and O atoms (Langmuir–Hinshelwood mechanism); no evidence for an Eley–Rideal mechanism is found.

The microscopic mechanisms of bimolecular surface reactions are traditionally described by two models [1]: The Langmuir–Hinshelwood (LH) mechanism assumes that both reactants are chemisorbed on the surface, whereas in the Eley–Rideal (ER) mechanism the reaction takes place between a chemisorbed particle and a second species which either collides directly from the gas phase or is held only weakly at the surface in a physisorbed state. A clear distinction on the basis of stationary measurements of the reaction kinetics is practically impossible, particularly if it is taken into account that saturation of the surface with one species does not necessarily inhibit the adsorption of the second one as is usually assumed in the formulation of kinetic rate laws for surface reactions. A closer inspection shows that the ultimate decision between the two possible mechanisms can only be made with knowledge of the mean surface residence times  $\tau_i$  of the reacting particles. For a species which is held at the surface with an adsorption energy of less than 10 kcal/mole (ER mechanism) above 300 K the residence time (and therefore also the time available for the reaction) will be less than  $10^{-6}$  s; if the reaction takes place by direct collision from the gas phase this time should be even shorter, viz. of the order of a vibrational period ( $\approx 10^{-13}$  s). If on the other hand, the time lag between the attachment of the reacting species to the surface and the formation of the reaction product is

considerably longer, this will be a clear indication of the LH mechanism, provided that the surface residence time of the product molecules is negligible.

The present communication is concerned with the catalytic oxidation of CO on palladium,  $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ , for which the LH mechanism appears to be well established [2], but for which additional evidence has been presented for a parallel ER mechanism, which, it has been maintained, should even dominate under stationary conditions at elevated temperatures [3]. Recent non-stationary studies with a Pd(111) surface, however, shed new light onto the possible modes of coadsorption and cast some doubt on the previous interpretation of the experimental findings [4]. In the present work this problem was therefore investigated with the modulated molecular beam technique [5]. The results allow, in our opinion for the first time, a clear distinction between different possible elementary processes for a surface catalyzed reaction.

A nozzle beam source provided a flux equivalent to a pressure of about  $10^{-7}$  torr at the Pd(111) target whose cleanliness and crystalline perfection were controlled with AES, LEED and He scattering. Molecules coming off from the surface were detected with a quadrupole mass spectrometer rotatable in the scattering plane. Background pressures of less than  $1 \times 10^{-10}$  torr were maintained in the system while the molecular beam was impinging on the surface. Phase shifts be-

tween the primary and the scattered beam were determined with lock-in techniques. For the modulation frequencies,  $\omega$ , used, transit times can be neglected.

It is well established from previous work that the reaction proceeds via dissociatively chemisorbed oxygen, this step on the other hand being inhibited by pre-adsorbed CO [2,3]. CO<sub>2</sub> once formed has a rather low adsorption energy so that its surface residence time is negligible under the present conditions [6]. The two reaction mechanisms are formulated in a simplified manner as follows:

(I) Langmuir–Hinshelwood



(II) Eley–Rideal



For the temperatures used in this study the desorption of O<sub>2</sub> as well as diffusion into the bulk are negligible [7]. With the ER mechanism no distinction is made between gaseous CO and an eventually physisorbed species since under the applied pressures and temperatures the surface concentration of the latter would be directly proportional to the CO pressure and its surface residence time would be below the limits of detection. Similar arguments hold with respect to the formed CO<sub>2</sub> molecules.

In the case of a modulated CO beam and a constant O<sub>2</sub> flux, the CO pressure at the target,  $p_{\text{CO}}$ , and the CO surface concentration are described as

$$p_{\text{CO}} = p_{\text{CO}}^0 + \alpha e^{i\omega t}$$

and

$$[\text{CO}_{\text{ad}}] = [\text{CO}_{\text{ad}}^0] + \beta e^{i\omega t}.$$

Substitution of these expressions in the kinetic rate laws for the above mechanisms under the assumption that  $d[\text{O}_{\text{ad}}]/dt = 0$  yields for the reaction rate of the LH mechanism:

$$\begin{aligned} d[\text{CO}_2]/dt &= k_4 [\text{O}_{\text{ad}}] \\ &\times \left[ [\text{CO}_{\text{ad}}^0] + \frac{k_1 \alpha e^{i(\omega t - \phi)}}{\{(k_2 + k_4 [\text{O}_{\text{ad}}])^2 + \omega^2\}^{1/2}} \right], \end{aligned} \quad (5)$$

with  $\tan \phi = \omega/(k_2 + k_4 [\text{O}_{\text{ad}}])$ .

The corresponding result for the ER mechanism is

$$d[\text{CO}_2]/dt = k_5 [\text{O}_{\text{ad}}] (p_{\text{CO}}^0 + \alpha e^{i\omega t}). \quad (6)$$

The LH mechanism thus predicts a temperature dependent phase lag for the CO<sub>2</sub> signal and for  $k_4 [\text{O}_{\text{ad}}] \ll k_2$ , which is in the temperature range studied satisfied even at moderate oxygen coverages, an apparent activation energy equal to the CO desorption energy (33 kcal/mole [7]), whereas no measureable phase shift should occur with the ER mechanism at all temperatures. The results shown in fig. 1 yield an apparent activation energy of 33 kcal/mole in perfect agreement with the LH mechanism. The activation energy for the surface reaction (3) is obtained from analysis of the measured CO<sub>2</sub> signal amplitude as described by eq. (5). The experimental data (fig. 2) are reasonably well reproduced by theory if the known adsorption energy for CO is taken into account and the pre-exponential  $\nu_2$  for CO desorption as well as the activation energy  $E_{\text{LH}}$  for reaction (3) are properly adjusted. For the latter thus a value of  $25 \pm 2$  kcal/mole results.

For the reverse case of a modulated O<sub>2</sub> beam and a constant CO flux, assuming  $d[\text{CO}_{\text{ad}}]/dt = 0$ , the LH mechanism predicts

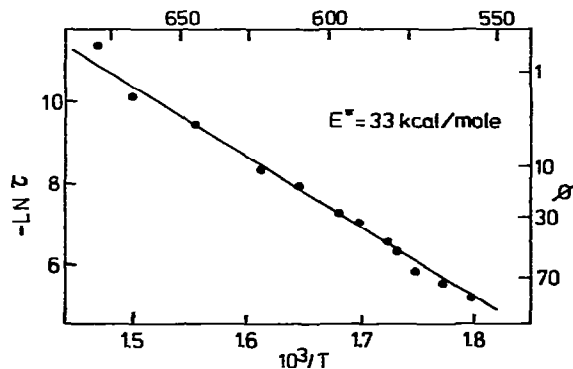


Fig. 1.  $\ln \tau$  and  $\phi$  versus  $1/T$  for a modulated CO beam.  $\omega = 779 \text{ s}^{-1}$ .

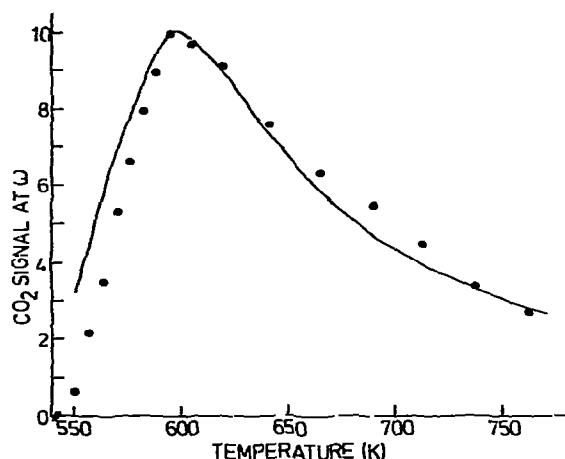


Fig. 2.  $\text{CO}_2$  signal at the modulation frequency  $\omega$  as a function of temperature.  $\omega = 124 \text{ s}^{-1}$ . The solid line is the frequency dependent part of the  $\text{CO}_2$  signal [eq. (5)] with  $k_2 = 14 \times 10^{14} \exp(-33000/RT) \text{ s}^{-1}$  and  $E_{\text{LH}}^* = 25 \text{ kcal/mole}$ . Experimental data are denoted by full circles.

$$\frac{d[\text{CO}_2]}{dt} = k_4 [\text{CO}_{\text{ad}}^0] \times \left[ [\text{O}_{\text{ad}}^0] + \frac{2k_3\alpha e^{i(\omega t - \phi)}}{(k_4^2 [\text{CO}_{\text{ad}}]^2 + \omega^2)^{1/2}} \right], \quad (7)$$

with  $\tan \phi_{\text{LH}} = \omega/k_4 [\text{CO}_{\text{ad}}]$ , whereas with the ER mechanism

$$\frac{d[\text{CO}_2]}{dt} = k_5 p_{\text{CO}} \left[ [\text{O}_{\text{ad}}^0] + \frac{2k_3\alpha e^{i(\omega t - \phi)}}{(k_5^2 p_{\text{CO}}^2 + \omega^2)^{1/2}} \right], \quad (8)$$

with  $\tan \phi_{\text{ER}} = \omega/k_5 p_{\text{CO}}$ .

Since for CO coverages well below saturation these are proportional to the CO pressure and may be written as  $[\text{CO}_{\text{ad}}] = \gamma p_{\text{CO}} \exp(E_{\text{CO}}/RT)$ , with  $E_{\text{CO}}$  the adsorption energy of CO, the explicit temperature dependence of the phase shifts is given by

$$\tan \phi_{\text{LH}} = (\omega/p_{\text{CO}} \nu_4) \exp[(E_{\text{LH}}^* - E_{\text{CO}})/RT] \quad (9)$$

and

$$\tan \phi_{\text{ER}} = (\omega/p_{\text{CO}} \nu_5) \exp(E_{\text{ER}}^*/RT). \quad (10)$$

( $E_{\text{LH}}$  and  $E_{\text{ER}}$  are the activation energies and  $\nu_4$  and  $\nu_5$  the pre-exponentials for reactions (3) and (4), respectively.)

Since  $E_{\text{CO}} > E_{\text{LH}}^*$  [6], the LH mechanism predicts a phase lag which increases from 0 to  $\pi/2$  with increas-

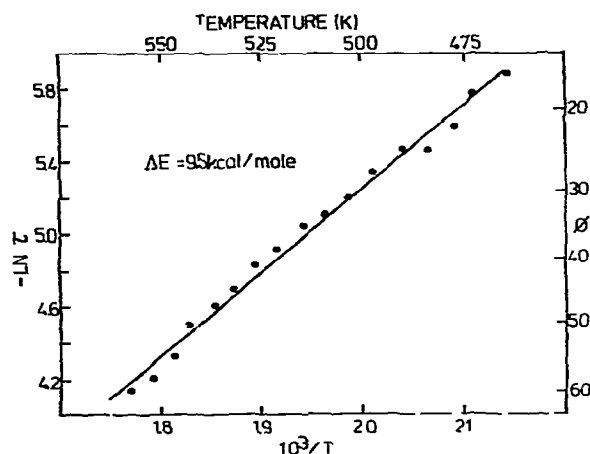


Fig. 3.  $\ln \tau$  and  $\phi$  versus  $1/T$  for a modulated  $\text{O}_2$  beam.  $\omega = 113 \text{ s}^{-1}$ . ( $\Delta E = E_{\text{LH}}^* - E_{\text{CO}}$ )

ing temperature whereas for the ER mechanism the phase lag should decrease from  $\pi/2$  to 0 with increasing temperature. The results reproduced in fig. 3 are in clear agreement with the LH mechanism and in contradiction to the ER mechanism. The activation energy  $E_{\text{LH}}$  obtained is  $23.5 \pm 2 \text{ kcal/mole}$  in good agreement with that derived on the basis of the data in fig. 2. It should be mentioned however that the activation energy for higher surface coverages is considerably lower [4,6] although the reaction also proceeds via a LH mechanism.

In summary, the surface residence times for CO associated with the catalytic oxidation of this molecule on Pd(111) lie in the range of  $10^{-2}$  to  $10^{-5} \text{ s}$  in the temperature range investigated. The magnitude and temperature dependence of this quantity clearly rule out an Eley-Rideal mechanism for this reaction. The main argument which has been presented in favour of an ER mechanism is that for  $T > 500 \text{ K}$  the reaction rate drops much less rapidly with increasing temperature than the stationary concentration of adsorbed CO [3]. This is, however, also in accord with the LH mechanism as is seen in fig. 2, since the decrease in  $[\text{CO}_{\text{ad}}]$  is partly compensated for by the increase of the rate constant for the surface reaction with increasing temperature. A more detailed discussion of the different aspects of this catalytic reaction will be presented elsewhere [4,6].

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