Abstract: Catalytic reaction between adsorbed oxygen and hydrogen on Rh(111)[a]

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We have studied both the kinetics of adsorption of O_2 by Rh(111) and the subsequent reaction of chemisorbed oxygen with $H_2(g)$ using Auger spectroscopy, low-energy electron diffraction (LEED), and thermal desorption mass spectrometry.

At 335 K, O_2 chemisorbs on Rh(111) into a mixture of ordered and disordered species.[1] By means of careful studies of the oxygen Auger intensity as a function of exposure to $O_2(g)$, it was found that the adsorption kinetics obey a Langmuir rate law involving a $(1 - \theta_0)$ factor, rather than exhibiting the expected $(1 - \theta_0)^2$ dependence for dissociative chemisorption (Fig. 1). This suggests that the chemisorption of O_2 by Rh(111) proceeds via a step involving a *single* Rh site and an O_2 molecule; subsequent dissociation is not rate controlling. There are numerous examples of the bonding of O_2 to transition metal atoms in the inorganic chemical literature.[2,3] Both peroxo complexes involving π-bonded O_2 and superoxo complexes bound end-on to metal atoms have been produced and studied spectroscopically. We suggest that a species of this kind may be a transient species in the chemisorption and dissociation of O_2 by Rh(111).

The adsorption of O_2 was studied also by LEED using a Faraday cup collector for measurement of beam intensity as a function of O_2 exposure. A "(2×2)" LEED pattern forms upon O_2 adsorption. Below $\theta_0 = 0.45$, the intensity of one of the overlayer beams $I_{(1,\overline{1/2})}$ was accurately proportional to θ_0^2, as expected for island formation with net pairwise attractive forces operating.[4] Beyond this point in coverage, more complex behavior is observed, with $I_{(1,\overline{1/2})}$ increasing more rapidly than θ_0^2 to a sharp maximum at $\theta_0 = 0.65$. This is designated the initial ordering region in Fig. 2. At still higher θ_0, a substantial decrease in $I_{(1,\overline{1/2})}$ occurs, followed by a twentyfold increase in $I_{(1,\overline{1/2})}$ above $\theta_0 \simeq 0.9$. This is designated the final ordering region in Fig. 2. We propose the following general picture to explain the intensity-exposure behavior for O_2 chemisorption on Rh(111) at 335 K:

stage 1: $\theta_0 \lesssim 0.45$, island growth with net pairwise attractive interactions;

stage 2: $0.45 \lesssim \theta_0 \lesssim 0.65$, three- or more-body attractive interactions giving accelerated ordering;

stage 3: $0.65 \lesssim \theta_0 \lesssim 0.90$, net many-body repulsive interactions giving loss of order;

stage 4: $\theta_0 \gtrsim 0.90$, final filling in of empty sites with optimally ordered overlayer.

It is interesting to note that on Ru(001), which is also a hexagonally symmetric surface, Madey *et al.*[5] observed very similar intensity-exposure behavior for an oxygen overlayer beam in the "(2×2)" pattern.

It was found that in the final ordering region, the rate of change of $I_{(1,\overline{1/2})}$ was accurately proportional to the rate of change of oxygen coverage; hence, the LEED intensity may be used for studying the kinetics of surface reactions involving the ordered oxygen in this region.

In Fig. 3, a plot is shown of the initial rate of ordered oxygen depletion, using $[dI_{(1,\overline{1/2})}/dt]$, as a function of the steady state P_{H_2}. The depletion process is *first order* in P_{H_2}. Consideration of the elementary surface reactions involved in the formation of $H_2O(g)$ suggests that the first step for H_2 interaction with *ordered oxygen* is
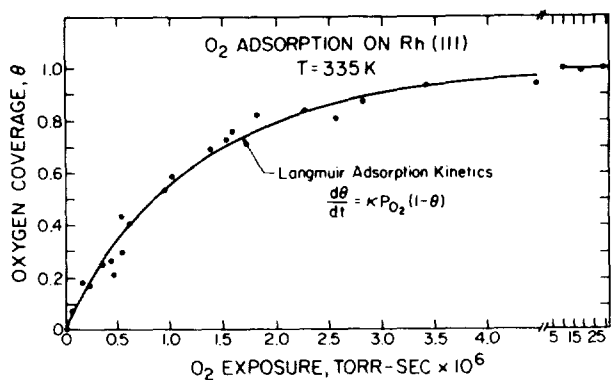
FIG. 1. Kinetics of O_2 adsorption on Rh(111) at 335 K. The fit to $(1 - \theta_0)$ kinetics has been found to be superior to a $(1 - \theta_0)^2$ fit.
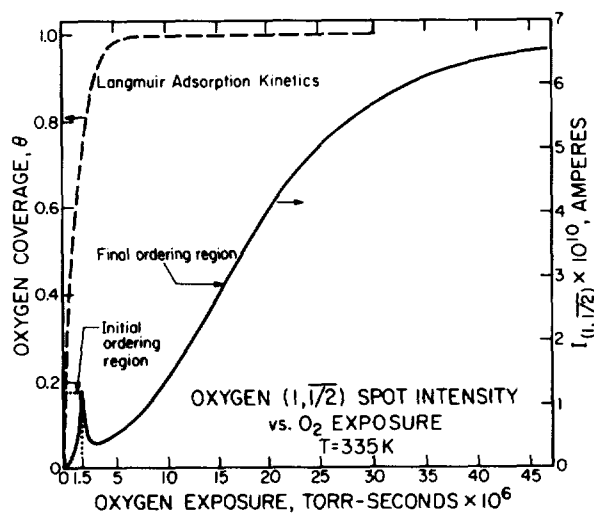

FIG. 2. Oxygen $(1,\overline{1/2})$ LEED beam intensity as a function of O_2 exposure at 335 K. The final ordering region occurs above $\theta_0 = 0.90$.

KINETICS OF REACTION OF
ORDERED OXYGEN WITH
H_2 ON Rh (III)

T = 335 K

Rate = κP_{H_2}

Rate = $\kappa P_{H_2}^{1/2}$
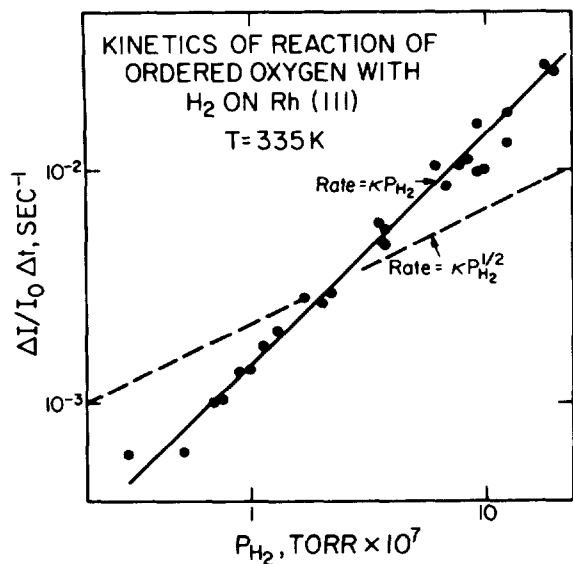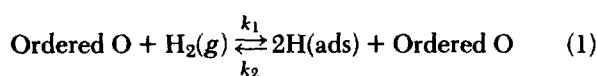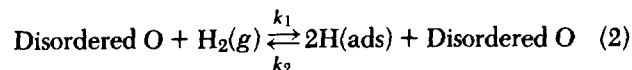
$\Delta I/I_0 \Delta t$, SEC^{-1}

P_{H_2}, TORR × 10^7

FIG. 3. Kinetics of reaction of ordered oxygen with $H_2(g)$ on Rh(111) at 335 K. The rate of reaction was measured by observing $|dI_{(1,\overline{1/2})}/dt|$ at various P_{H_2}.

$$\text{Ordered O} + H_2(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2H(\text{ads}) + \text{Ordered O} \qquad (1)$$

with $k_2 = 0$. Ordered O provides *trap sites* for H(ads), preventing the k_2 process and giving first-order kinetics in P_{H_2}. By studying the rate of reaction in the temperature region, $313 \text{ K} \leq T \leq 457 \text{ K}$, the activation energy was measured to be 5.3 ± 0.3 kcal/mol-$^{-1}$. For each reaction event, order is lost from a domain of which the area is approximately 300 Å^2.

Auger spectroscopy was used also to monitor surface oxygen coverage during reaction with $H_2(g)$. The rates measured in this fashion in a particular range of P_{H_2} are thought to be determined mainly by the reaction of *disordered* oxygen with $H_2(g)$. Here, the kinetics are found to be *one-half* order in P_{H_2}, consistent with a first step:

$$\text{Disordered O} + H_2(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2H(\text{ads}) + \text{Disordered O} \qquad (2)$$

where $k_2 > 0$.

This system provides an excellent example of the influence of geometrical factors in determining the kinetics of a heterogeneously catalyzed surface reaction.

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