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 \(\text{O}_2\) by Rh(111) and the subsequent reaction of chemisorbed oxygen with \(\text{H}_2\) using Auger spectroscopy, low-energy electron diffraction (LEED), and thermal desorption mass spectrometry.

At 335 K, \(\text{O}_2\) 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 \(\text{O}_2\), it was found that the adsorption kinetics obey a Langmuir rate law involving a \((1 - \theta_0)^2\) factor, rather than exhibiting the expected \((1 - \theta_0)^3\) dependence for dissociative chemisorption (Fig. 1). This suggests that the chemisorption of \(\text{O}_2\) by Rh(111) proceeds via a step involving a single Rh site and an \(\text{O}_2\) molecule; subsequent dissociation is not rate controlling. There are numerous examples of the bonding of \(\text{O}_2\) to transition metal atoms in the inorganic chemical literature.\(^2,3\) Both peroxo complexes involving \(\pi\)-bonded \(\text{O}_2\) 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 \(\text{O}_2\) by Rh(111).

The adsorption of \(\text{O}_2\) was studied also by LEED using a Faraday cup collector for measurement of beam intensity as a function of \(\text{O}_2\) exposure. A \((2 \times 2)\) LEED pattern forms upon \(\text{O}_2\) adsorption. Below \(\theta_0 = 0.45\), the intensity of one of the overlayer beams \(I_{(1,1/2)}\) was accurately proportional to \(\theta_0\) as expected for island formation with net pairwise attractive interactions.\(^4\) Beyond this point in coverage, more complex behavior is observed, with \(I_{(1,1/2)}\) increasing more rapidly than \(\theta_0\) to a sharp maximum at \(\theta_0 = 0.65\). This is designated the initial ordering region in Fig. 2. At still higher \(\theta_0\), a substantial decrease in \(I_{(1,1/2)}\) occurs, followed by a twentyfold increase in \(I_{(1,1/2)}\) above \(\theta_0 \approx 0.9\). This is designated the final ordering region in Fig. 2. We propose the following general picture to explain the intensity-exposure behavior for \(\text{O}_2\) chemisorption on Rh(111) at 335 K:

- Stage 1: \(\theta_0 \leq 0.45\), island growth with net pairwise attractive interactions;
- Stage 2: \(0.45 < \theta_0 \leq 0.65\), three- or more-body attractive interactions giving accelerated ordering;
- Stage 3: \(0.65 < \theta_0 \leq 0.90\), net many-body repulsive interactions giving loss of order;
- Stage 4: \(\theta_0 \geq 0.90\), 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 \((2 \times 2)\) pattern.

It was found that in the final ordering region, the rate of change of \(I_{(1,1/2)}\) 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 \(\frac{dI_{(1,1/2)}}{dt}\), as a function of the steady state \(P_{\text{H}_2}\). The depletion process is first order in \(P_{\text{H}_2}\). Consideration of the elementary surface reactions involved in the formation of \(\text{H}_2\) \(\text{O}_2\) suggests that the first step for \(\text{H}_2\) interaction with ordered oxygen is

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**Fig. 1.** Kinetics of \(\text{O}_2\) 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 \((1,1/2)\) LEED beam intensity as a function of \(\text{O}_2\) exposure at 335 K. The final ordering region occurs above \(\theta_0 = 0.90\).
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 $\frac{d[1]}{dt}$ at various $P_{H_2}$.

Ordered O + $H_2(g) \overset{k_1}{\rightarrow} 2H(ads) + \text{Ordered O} \quad (1)$

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 K $\leq T \leq 457$ K, the activation energy was measured to be $5.3 \pm 0.3$ kcal/mol$^{-1}$. For each reaction event, order is lost from a domain of which the area is approximately $300 \text{Å}^2$.

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:

$$\text{Disordered O} + H_2(g) \overset{k_1}{\rightarrow} 2H(ads) + \text{Disordered O} \quad (2)$$

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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