

phere as indicated by its light blue color, but they are the part of an oxide on silica gel as distinctly shown by X-Ray diffraction. More precise investigations in the kinetics and mechanism of the oxidation over the Cu-Y and for other olefins are in progress.

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Interaction of Oxygen and Butene with Gold*

In previous studies (1) of the catalytic activity of polycrystalline gold for the isomerization of 1-butene, the degree of isomerization was found to increase in the presence of hydrogen, while the addition of oxygen completely suppressed isomerization. To obtain a better understanding of the inherent catalytic properties of a non-transition metal, such as gold, for non-skeletal isomerization, a series of measurements was carried out on the interaction of O₂ and 1-butene on gold foil ribbons in an ultrahigh vacuum (UHV) apparatus.

The apparatus used in these studies consisted of two chambers separated by a remote-control shutter and evacuated by

separate ion-getter pumps (2). Such an arrangement allowed pretreatment of the catalyst in a separate chamber, preceding the admission of various reactants. The gold catalyst,† a polycrystalline foil ribbon (0.002 in. thick, 11 cm² in geometric area, C.P. grade), was supported in one of the chambers of the UHV system by two electrodes through which an electric current could be passed for heating the ribbon.

Before a sorption experiment the ribbon was cleaned by flash desorption (1075°K for 2 min) and then allowed to cool to the reaction temperature for 3 min, at a background pressure of 5×10^{-9} torr. The rate

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† The gold foil was obtained from Wildberg Bros., San Francisco, Calif. It contained 0.065 wt % carbon.

of sorption and the total mass of gas sorbed were monitored with a mass analyzer and ion gauges. The surface temperature of the gold ribbon was measured optically,* and the observed brightness temperatures were corrected on the basis of an emissivity of 0.1 for metallic gold. The temperatures reported refer to the central portion of the specimen. Studies of the rate of interaction of the gases under investigation with the gold ribbon were carried out under constant-flow conditions with suitable corrections applied to account for the sorption of gas by other surfaces within the specimen chamber.

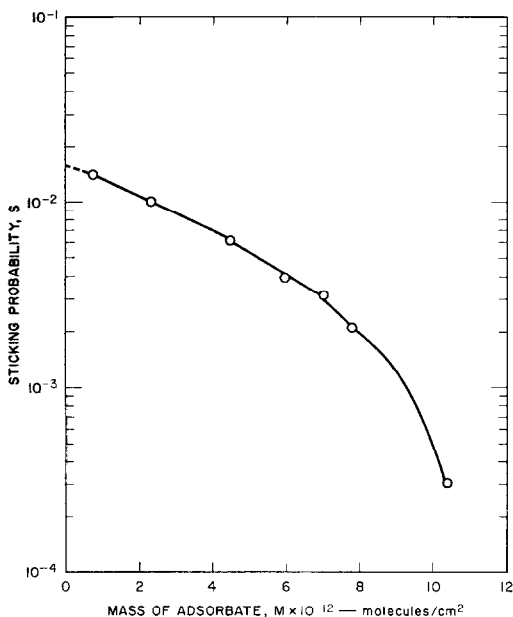


FIG. 1. Sticking probability of oxygen on polycrystalline gold as a function of surface coverage (ribbon temperature = 473°K, $P_{O_2} = 1.1 \times 10^{-7}$ torr).

The initial rate of interaction of O_2 with clean gold, expressed as the sticking probability, S , was found to be 2×10^{-2} . As is apparent in Fig. 1, this rate diminished with coverage. However, the rate exhibited little variation with temperature over the range studied. Under our experimental conditions, the total surface density of sorbed oxygen amounted to a small fractional cov-

* Huggins Infrascoper radiation thermometer.

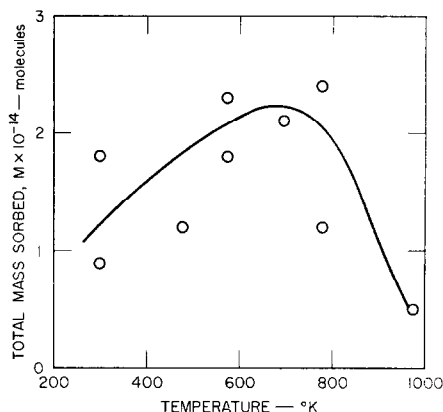


FIG. 2. Total mass of oxygen sorbed as a function of gold ribbon temperature.

erage of the gold surface (less than 0.05). The total mass of molecular oxygen sorbed as a function of the gold ribbon temperature is shown in Fig. 2.

Similar measurements with 1-butene (at 1×10^{-7} torr) on a gold ribbon in the temperature range 300 to 673°K demonstrated the complete absence of a sorption process on a flash-cleaned surface (1075°K). In a subsequent experiment, the gold surface was exposed to oxygen before the admittance of 1-butene. The ribbon at 1075°K was first exposed to oxygen at 1×10^{-7} torr. Then the ribbon temperature was lowered to a specified value in the oxygen environment for 2 min. Following evacuation of the chamber to 5×10^{-9} torr for 1 min, butene-1 was admitted to a pressure of 1×10^{-7} torr. Under these conditions the mass of butene sorbed on the gold was observed to be dependent on its temperature (Fig. 3). While no interaction was noted at

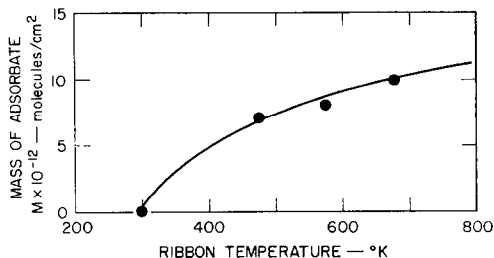


FIG. 3. Sorption of butene-1 on oxygen-treated gold as a function of temperature ($P_{Bu-1} = 1.0 \times 10^{-7}$ torr).

room temperature, the sorption of 1-butene could be followed at higher ribbon temperatures by monitoring the peak intensity at $\text{amu } 56$.

Desorption experiments were also carried out by raising the ribbon with its adsorbate to elevated temperatures. During these experiments it appeared that 1-butene underwent a chemical reaction associated with a net mass loss from the gas phase.

The results obtained in the study of the Au-O₂ system were near the limit of resolution of the apparatus employed. Consequently, the degree of precision is low, yet certain conclusions may be drawn which are of consequence in the interpretation of the observed catalytic properties of gold (1). The extent of saturation surface coverage with oxygen is low (Fig. 1) and a maximum value is reached at a temperature near 700°K. This observed change in the mass sorbed as a function of surface temperature (at $T < 700^\circ\text{K}$) suggests an endothermic heat of adsorption of oxygen on gold and therefore an activated step for adsorption.

At 700°K the observed initial rate of sorption of oxygen amounts to 3×10^{11} molecules/cm²-sec, in good agreement with the value reported by other investigators (3) who employed higher oxygen pressures. In addition, comparison of our data and those of Ref. (3) suggests that the extent of saturation surface coverage is a function of the oxygen gas pressure.

The absence of any sorption of 1-butene

on clean gold but its interaction with sorbed oxygen suggests that catalytic reaction does not require the presence of both reactants as chemisorbed species on adjacent metallic sorption sites. At the highest surface coverage with oxygen (Fig. 1) the total mass of 1-butene consumed from the gas phase yields a ratio of $\text{O}/\text{C}_4\text{H}_8 = 4$. In all likelihood, partial oxidation of the olefin takes place with the formation of surface-sorbed intermediates. Such species may be responsible for the isomerization of 1-butene reported in Ref. (1); in these experiments pretreatment of the gold catalyst with oxygen was employed to activate the catalyst for the isomerization process. The data presented lend further emphasis to the utility of UHV studies for the elucidation of catalytic reactions.

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