

NOTES

A Comparative Study of the Rapid Adsorption of Oxygen by Silver and Gold

The interaction between oxygen and gold has received little attention as there has been a general belief that oxygen does not adsorb on gold. Trapnell (1) stated in 1953 that oxygen did not chemisorb on gold films at temperatures up to 0°C, although it was physically adsorbed at -183°C. Other workers (2-4) have come to the same conclusion. There is, however, evidence (5-11) that oxygen must chemisorb on gold, especially during oxidation reactions (6, 7). Kul'Kova and Levchenko (8) observed that chemisorption occurred in the temperature range 50-400°C with an activation energy of 3200 cal/mole. They found the rate of uptake to be very slow at 50°C, indicating that at 0°C adsorption would be observed only after a long period of time. It should be mentioned that the adsorption studies to date were carried out in static systems where the amount of oxygen was large compared to the available surface area of gold, so that any initial rapid uptake occurring on a fraction of the surface would not be detected.

Recent investigations in this laboratory on the decomposition of nitrous oxide on silver, gold, and a series of silver-calcium alloy catalysts (12) in the temperature range 200-500°C indicated that the reaction was inhibited on each catalyst by the adsorbed product oxygen. These results were expected for silver (13, 14) and the alloys (14), but not for gold (2, 4). Previous unpublished results (15) did, however, indicate that the reaction was also inhibited on gold. Because of the disagreement in the literature as to whether or not oxygen was adsorbed on gold, and as a result of the

nitrous oxide studies, the adsorption of molecular oxygen on a gold powder in the temperature range from -89 to 450°C using the gas chromatographic microreactor technique was investigated. For comparison, identical experiments were performed on Ag.

EXPERIMENTAL METHODS

The apparatus consisted of a gas chromatograph using purified helium as the carrier gas, and a vacuum system. The powdered catalysts, which were sintered to a porous mass at 500°C, rested on a slight constriction of the reactor U-tube. Glass wool could not be used to support the catalyst as it also adsorbed oxygen. By detecting the amount of oxygen not adsorbed from a pulse of a known pressure and volume, the oxygen uptake by the catalyst could be obtained at any temperature. The present method therefore allowed only the detection of an initial rapid uptake from a pulse; it was not possible to study slow equilibrium adsorption. 2.000 g of gold, 0.168 g of silver, each of 99.999% purity, were used in the adsorption studies. The surface areas of the two metals were very small and within experimental error were identical at 0.15 m²/g as determined by a nitrogen BET microtechnique.

Prior to adsorption studies the metals were reduced in flowing hydrogen (ca. 50 ml/min) at 500°C for 1 hr, after which the reactor was evacuated to 10⁻⁶ Torr for 1 hr. The temperature was then reduced to the desired temperature for adsorption studies. The metals were rereduced at

500°C after each adsorption experiment, except where noted.

RESULTS

The amount of oxygen adsorbed from a 1 Torr pulse of oxygen (equiv to 8.65×10^{-8} moles) passed over gold is shown in Fig. 1. At each temperature this is the uptake after the metal had been reduced at 500°C. The results for silver are shown in Fig. 2. The decrease in adsorption upon the passage of several consecutive pulses over gold at 0°C is given in Table 1. No reduction was carried out between these pulses.

TABLE 1
MOLES OF O₂ ADSORBED ON Au AT 0°C

Pulse no.	O ₂ pressure (Torr)	O ₂ injected ($\times 10^7$ moles)	O ₂ adsorbed ($\times 10^7$ moles)
1	1.090	0.942	0.288
2	1.000	0.865	0.067
3	0.945	0.818	0.028
4	0.903	0.780	0.012

The advantage of this method over a static method is apparent in its ability to detect small quantities of gas adsorption and allow for a short contact time. The contact time in the present case was about

2 sec. The rapid decrease in adsorption as more oxygen contacts the metal, can only serve to emphasize why a static method would be unable to detect any adsorption at low temperatures.

It is immediately obvious that oxygen is adsorbed on gold. The amount adsorbed is, however, considerably smaller than would be expected for an equivalent weight of silver.

Both silver and gold exhibit the normal maximum in the oxygen isobar. It must be remembered that the results shown are for a dynamic method involving the uptake of oxygen from one pulse. The temperature of the maximum is therefore higher than would be observed in equilibrium studies. The most interesting feature of the isobars is the occurrence of a second maximum at a lower temperature. This maximum occurs on silver between 0–25°C, but is not very prominent. There has been no mention in the literature of this phenomenon on silver, although Czanderna (16) states that "quantitative changes" in the oxygen adsorption occur at about 25 and 100°C. This worker determined the rate of adsorption, but could not follow the initial rate in the first few seconds, and did not offer an explanation for the "quantitative change" at 25°C.

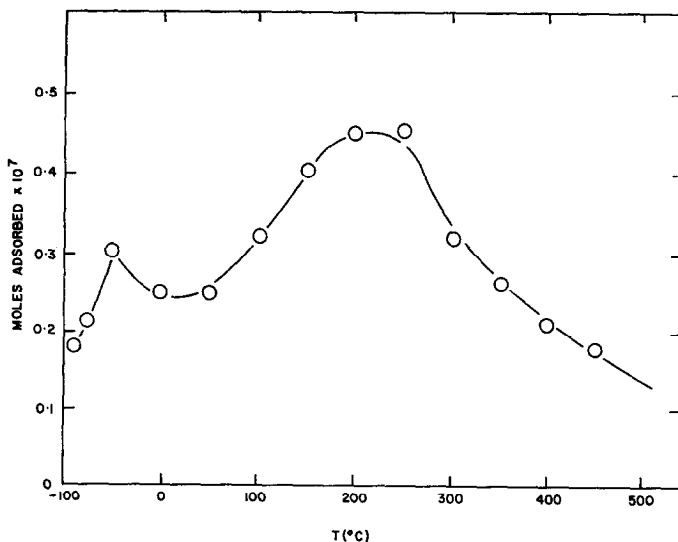


FIG. 1. The uptake of oxygen by gold.

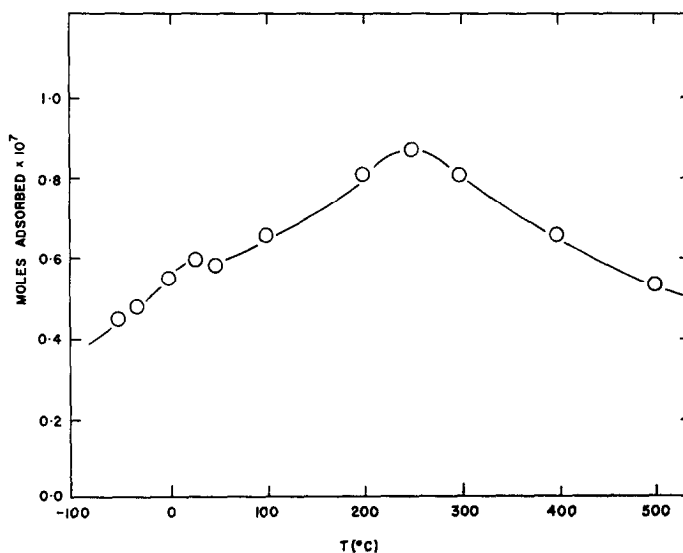


FIG. 2. The uptake of oxygen by silver.

The second maximum occurs on gold at about -50°C ; this was a most unexpected result and one for which there is as yet no explanation. This maximum is reproducible, it is also more prominent than is the case on silver. In a series of experiments where four pulses of oxygen were passed over gold at -50°C , the total uptake was greater than that at 0°C , the latter being indicated in Table 1. Evacuating the reactor and pumping for an extended period at -50°C failed to remove any of the adsorbed gas; raising the temperature from -50 to 0°C resulted in a slight desorption, but this was not equal to the difference between the uptake at these two temperatures. The evidence is thus indicative of a firmly chemisorbed oxygen species at low temperatures.

It must be emphasized that this work was motivated by the results of the investigation of the decomposition of nitrous oxide on these metals, and was only a small part of the project. The experiments demonstrate the ability of the microreactor technique to provide valuable information when the amount of adsorbate is small compared to the available adsorbent surface. The flow method allows one to observe an event during a short interval; with suitable modification of the apparatus adsorption could

be allowed to occur over an extended period of time.

Further research is being undertaken to investigate the adsorption of oxygen on gold, particularly during the initial stages of the adsorption.

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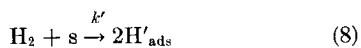
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Methanation of CO on a Ni Catalyst

In a recent article (1) the methanation of CO on some Ni catalysts was studied. A mechanism was proposed, the rate of hydrogen adsorption being the rate determining step. The adsorption could take place in two ways in parallel:



The equation numbers refer to the numbers in the above article.

The methanation rate was determined by the rate with which hydrogen in the "active" states H'_{ads} and H''_{ads} , could be supplied to reaction with CO adsorbed on dual sites. With nearly all sites covered by CO and H_2 adsorbed on dual sites and Eq. (8) determining the rate, the rate equation became:

$$r_1 = k' p_{\text{H}_2}^{0.5} / \left(1 + A \frac{p_{\text{CO}}}{p_{\text{H}_2}} \right)^{0.5}, \quad (13)$$

and in the case of Eq. (9) determining the rate:

$$r_2 = k'' / \left(1 + A \frac{p_{\text{CO}}}{p_{\text{H}_2}} \right)^{0.5}. \quad (14)$$

In the previous article, the pressure dependence was tested in the range 1–15 atm

absolute where, however, a single rate equation with $p_{\text{H}_2}^{0.15}$ in the numerator fitted as well with the experiments (within the experimental errors) as did the rate expressed by the sum of Eqs. (13) and (14) with the ratio $k':k'' = 1:4$.

New experiments with catalyst No. 1 in a pressure range extended to 110 atm have shown that the pressure dependence at high pressures actually approaches proportionality to the square root of the total pressure (at constant CO concentrations). Typical experiments with catalyst No. 1 are presented in Fig. 1; these experiments fit well with either of the rate equations:

$$r = 0.048(1 + 0.2 p_{\text{H}_2}^{0.5}) \quad \text{i.e., } k':k'' = 1:4,$$

or

$$r = 0.041(1 + 0.25 p_{\text{H}_2}^{0.5}) \quad \text{i.e., } k':k'' = 1:5.$$

Besides, the numerator activation energies at 1 atm and 90 atm were found to be nearly equal (24–26 kcal/mole) in the temperature range 220–270°C with catalyst No. 1 and 1% CO in H_2 . This means that the ratio $k':k''$ is practically independent of the temperature.

The two hypothetical forms of active hydrogen, H'_{ads} and H''_{ads} , are possibly formed with different preference on different crystallographic planes and are dis-