

STUDIES ON CHEMISORPTION OF OXYGEN ON COPPER ORTHOVANADATE

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Kinetics of chemisorption of oxygen has been measured by the constant volume method on copper orthovanadate (a) preheated at 350°C in vacuo and (b) preheated with hydrogen at 130°C. Arrhenius activation energy for the former increases with surface coverage at 138°C–239°C, while for the latter it generally decreases and becomes negative at higher coverages.

An attempt has been made to explain the negative activation energy on the basis of the Knudsen diffusion.

INTRODUCTION

The system copper oxide—vanadium pentoxide loses oxygen at higher temperatures even in an oxygen atmosphere leading to the formation of a series of copper vanadium bronzes, the compositions of which are dependent upon the temperature and copper content of the system (Brisi and Molinari 1958). Particularly, in case of copper orthovanadate, $3\text{CuO} \cdot \text{V}_2\text{O}_5$, the formation of a nonstoichiometric compound, $3\text{CuO} \cdot \text{V}_2\text{O}_4$, has been observed (Strupler 1962). In this paper the authors have presented the studies on the chemisorption of oxygen on copper vanadate activated by two different methods—(A) by evacuation and (B) by pretreatment with hydrogen followed by evacuation.

EXPERIMENTAL

1. Preparation of the samples

(a) *Sample A* — $\text{Cu}_3(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$ was precipitated at room temperature from 0.3 (M) copper nitrate solution with saturated ammonium metavanadate solution (about 3 gm/litre). The characterisation of the sample was done by chemical analysis and X-ray diffraction studies (Bhattacharyya *et al.* 1968).

The powdered sample between—100. to + 120 mesh size B. S. was activated by evacuation at 350°C under a pressure of 10^{-5} torr for 60 hours.

(b) *Sample B*— Sample A prepared thus was treated in the volumetric adsorption apparatus with pure and dry hydrogen at 130°C under a constant pressure

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of 40 cm. Addition of hydrogen was continued in doses until equilibrium was established, then the system was evacuated at 300°C for 5 hour, after which it was cooled to 130°C and again treated with hydrogen in the same way as above. The process was repeated several times until the volume of hydrogen uptake up to the establishment of equilibrium at 130°C and 40 cm pressure was quantitatively reproducible. Sample A, thus pretreated with hydrogen, constituted sample B.

2. Apparatus and procedure

The apparatus used for the adsorption measurement was a conventional volumetric BET unit comprising of a gas burette, manometer and a catalyst tube.

About 3 gm of sample A and 2.5 gm of sample B were taken and all the measurements were carried out on the same sample. Before each experiment, as a standard procedure, the system was evacuated at 400°C for 6 hours. The kinetics of chemisorption of oxygen on each sample was measured under constant volume conditions and the difference in pressure (Δp cm) was noted at different time intervals.

RESULTS AND DISCUSSIONS

Part I : Sample A—The BET surface area of the sample is 4.75 m²/gm. At 100°C the rate of oxygen uptake is too slow to be measured even at an oxygen pressure of 20 cm. But as temperature increases, the rate increases rapidly and at 239°C the rate of adsorption can be measured even at a pressure of 1.40 cm. The attainment of adsorption equilibrium at any temperature is extremely slow. At 239°C and 15 cm initial pressure there occurs considerable pressure change even after 2000 min. The regeneration of the surface involves much difficulty and reproducible kinetic data are often obtained only after prolonged and repeated evacuations at 400°C.

Kinetics of chemisorption has been measured at 198°C and 3.85 cm initial pressure and at 239°C and 1.40, 3.85, 9.36 and 15.10 cm initial pressures. The volume of oxygen adsorption at a given equilibrium pressure increases from 198° to 239°C. Fig. 1 represents the pressure *vs.* time plots for all the experiments. The kinetic data obey the integrated Elovich equation (Cimino *et al.* 1960). The Arrhenius activation energy calculated in the temperature range of 198°–239°C at an initial ambient pressure of 3.85 cm has been plotted against Δp cm (pressure difference between the two limbs of the manometers, one limb of which is exposed to the atmosphere) in Fig. 2. It indicates a nearly linear increase of activation energy with coverage. Initially the activation energy is quite low at lower coverage (about 2.7 K cal/mole at $\Delta p = 0.20$ cm) but it attains a high value at higher coverage (about 16.4 Kcal/mole at $\Delta p = 0.90$ cm).

Enikeev *et al.* (1959) have attributed a linear increase in activation energy with coverage to a linear increase in electron work function with the same. According to these authors, Elovich equation is followed in this case and the nature of chemisorption is depletive. As copper vanadate at high temperature is shown to

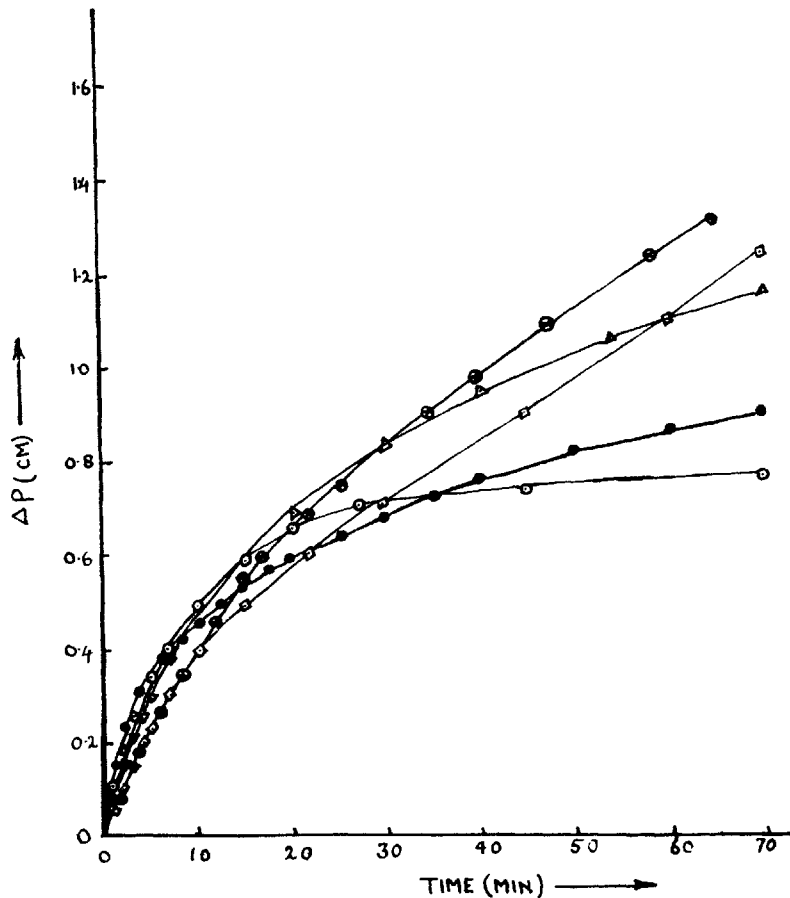


FIG. 1. Pressure vs. Time for experiments —●—●— 198°C 3.85 cm ;
 —○—○— 239° 1.40 ; —△—△— 239° 3.85 ; —□—□— 239° 9.36 ;
 —⊗—⊗— 239° 15.10.

be oxygen deficient, the non-stoichiometry being dependent on temperature (Brisi and Molinari 1958), the slow chemisorption of oxygen on sample A may involve the interaction of the adsorbed oxygen molecule with the vacant surface anion sites, ultimately leading to the build-up of the oxide lattice.



The O^- ions are not removed from the surface rapidly and a Schottky barrier of negative charge is gradually built up at the surface as adsorption proceeds, ultimately leading to a linear increase of activation energy with coverage (Hauffe 1957).

Part—II : Sample B—On pretreatment with hydrogen the BET surface area of the sample B is 10.92 m²/gm.

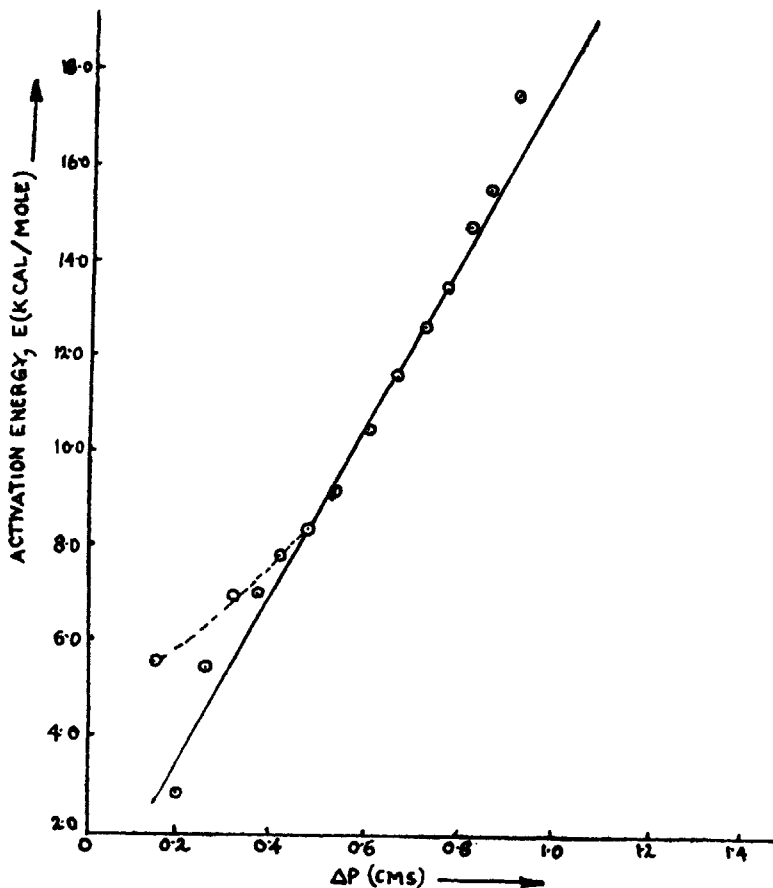


FIG. 2. Arrhenius activation energy vs. Pressure.

Kinetics of oxygen chemisorption on sample B have been measured in the temperature range of 0° – 253°C at an initial pressure of 12.0 cm. In all cases, even at 0°C , the rate of oxygen uptake is very rapid. However, the instantaneous adsorption is followed by further adsorption at measurable rate and the equilibrium is established in 2–3 hour. The pressure vs. time plots for all temperatures are shown in Fig. 3. The kinetic data obey the logarithmic rate equation of Elovich. The Elovich Plots (not shown in Fig.) show one break at all temperatures except at 0°C , the rate of the 2nd step being higher than that of the first.

From the kinetic plots (Fig. 3) it appears that the rate has a negative temperature coefficient at 98°C and above. The Arrhenius activation energies are given in Table I. Only at 0° – 31°C the activation energy is 10–15 K cal/mole and increases with coverage at low coverages. But at all coverages in higher temperatures the activation energy decreases with coverage and ultimately becomes negative. However, the decline of activation energy with coverage is restricted to lower temperature

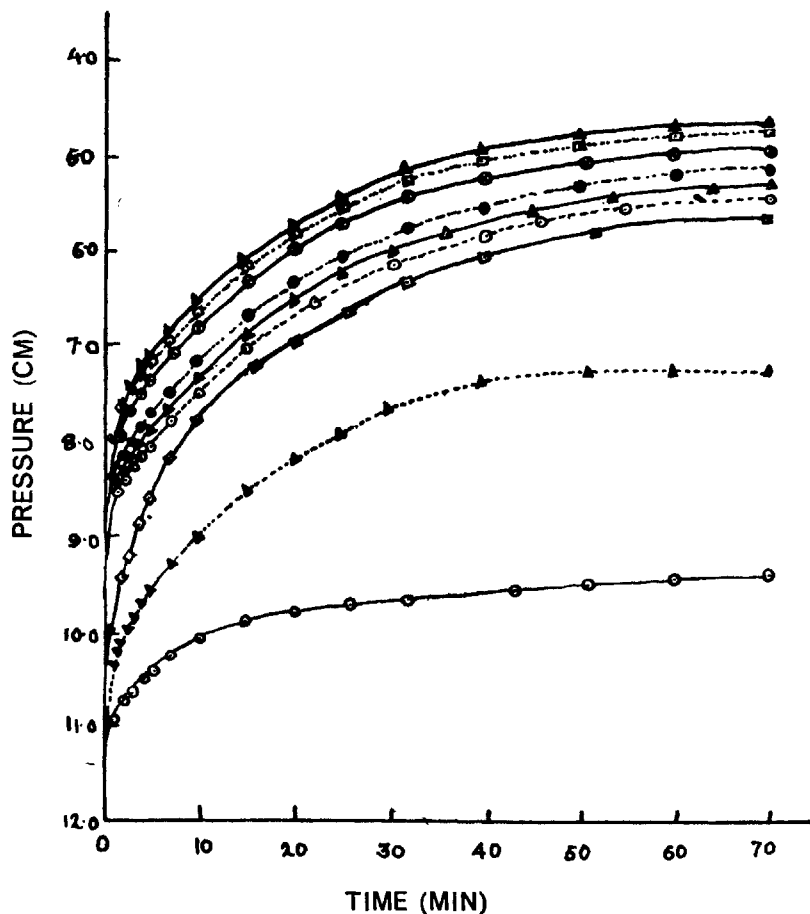


FIG. 3. Pressure vs. Time for all temperatures



only, namely, upto 98°C. Beyond that though activation energy is negative, but, relatively speaking, it increases with coverage.

The occurrence of negative activation energy with coverage has been reported and explained by several workers (Sastri and Ramanathan 1952; Taylor and Liang 1947; and Leibowitz *et al.* (1958). But none could explain the phenomenon in a constant volume system and the origin of Elovich equation in such a case.

According to the model of Sutherland and Winfield (1953) the rate determining step in case of rapid chemisorption (so that adsorption equilibrium between the gas and the pore walls prevails all the time) is the Knudsen flow of gas molecules into the interparticle pores. The model gives rise to the Elovich equation in a constant

TABLE I

Activation energy for oxygen chemisorption on sample—B (E in K Cal/mole)

Mole adsorbed per gm $\times 10^5$	0°–31°C	31°–51°C	51°C–77°C	77°–98°C	98°–136°C	136°–167°C	167°–206°C	206°–253°C
1.6	10.12							
2.0	11.81	3.87						
2.4	15.27	4.48						
2.8		3.10						
3.4		2.35	13.95					
4.0		1.34	12.28	6.25	—	—10.57	—3.80	—5.14
4.8		—0.65	8.26	4.87	—1.18	—7.99	—1.33	—1.81
5.7		—2.32	6.65	2.83	—0.53	—5.26	—1.47	—0.96
6.4		—3.39	—	2.53	—0.07	—5.06	—2.17	—2.02

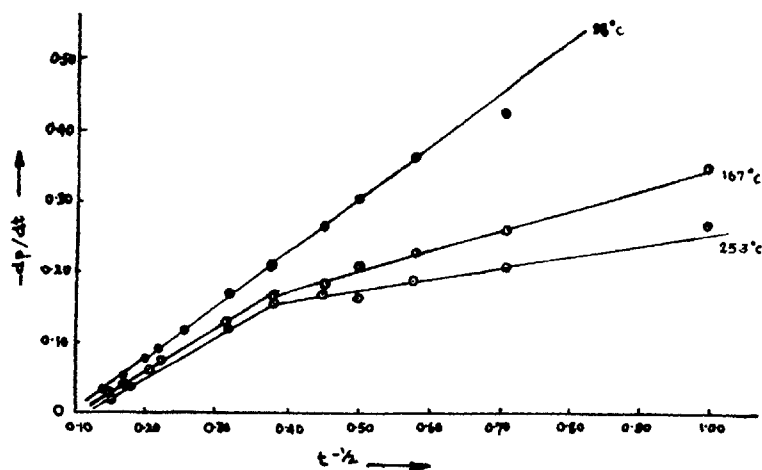


FIG. 4.

volume system and provides with a theoretical method for the evaluation of Elovich constant, α , from the pore character of the adsorbent. According to these authors,

$$-\frac{dp}{dt} = X \times \frac{T^{3/4} \exp(Q/2RT)}{t^{1/2}} \quad \dots\dots(1)$$

where K = proportionality constant.

Hence the rate has a negative temperature coefficient, when the variation of $T^{3/4}$ is negligible in comparison with that of $e^{Q/2RT}$. Fig. 4 represents the plot of $-dp/dt$ (calc. graphically from Fig. 3) $t^{-1/2}$ for kinetic data at 98°, 167° and

253°C. In view of the error in the graphical evaluation of $-\frac{dp}{dt}$ values, the agreement can rather be described as good. As is expected, the slope of the plots (*i.e.*, $\text{const.} \times e^{Q/2RT}$) increases as temperature decreases, but at higher temperatures the plots have one break. It is likely that the change in the slope in Fig. 4 is due to a change in Q . In the second stage the heat of adsorption Q_2 is not only greater than that at the first stage, Q_1 , but also $Q_2 \gg RT$ so that change in T has very little influence in changing the slope at different temperatures.

Morette and Strupler (1962) have observed that $\text{Cu}_3(\text{VO}_4)_2$ on being treated with hydrogen in a static system at 130°C is reduced to a mixture of Cu and V_2O_3 . The reduction is complete through the solid state reaction between metallic Cu and V^{5+} . So it may be expected that oxygen adsorption on sample B at higher temperatures is essentially the oxidation of either Cu or V_2O_3 or both. But the ease with which the surface is regenerated in comparison with sample A and reproducible kinetic data are obtained effectively rules out any immediate irreversible reaction occurring on the surface. However, the oxygen adsorbed may gradually be transformed into O^{2-} ions which become part of the oxide lattice.

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