

Studies on Kinetics of Chemisorption of Oxygen and Electrical Conductivity Changes on Vanadium Pentoxide Catalysts

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Vanadium pentoxide prepared by the decomposition of vanadyl oxalate (catalyst I) has been reported by Bhattacharyya and co-workers to have better catalytic activity for certain oxidation reactions than the one prepared by the decomposition of ammonium metavanadate (catalyst II). The kinetics of chemisorption of oxygen and the accompanying changes of electrical conductivity have now been studied on V_2O_5 prepared by the two different methods.

The oxygen chemisorption kinetics in the temperature range 100–400°C could be well described by the Elovich equation. The rate and amount of oxygen adsorbed on catalyst I was almost double that on catalyst II. A decrease in electrical conductivity with increasing oxygen pressure was noted for both catalysts. However, the rate of decrease of conductivity, under similar conditions, was always more for catalyst I. These observations can probably be related to the greater activity of catalyst I.

INTRODUCTION

Vanadium pentoxide is widely known as a very important catalyst for numerous oxidation processes. Investigations carried out by Bhattacharyya and co-workers (1–3) have shown that vanadium pentoxide catalyst (catalyst I) prepared by the decomposition of vanadyl oxalate exhibits a much greater catalytic activity for reactions like oxidation of *o*-xylene and naphthalene to phthalic anhydride and maleic anhydride than that prepared by the decomposition of ammonium metavanadate (catalyst II).

Until recently, a number of investigations have been carried out by various workers to assess the defect nature of the vanadium pentoxide catalyst. For example, Simard *et al.* (4) envisaged the surface of the active vanadium pentoxide catalyst as a dynamic one involving continuous

changes from orthorhombic V_2O_5 -like structures to monoclinic $V_2O_{4.34}$ -like structures and vice versa. The X-ray diffraction studies of Ioffe and Patrino (5) indicated the presence of various nonstoichiometric phases between the compositions V_2O_5 and V_2O_4 in an active vanadium pentoxide catalyst. Also Gillis (6) reported the formation of the nonstoichiometric phase $V_{1.2}O_{2.6}$ by the ready liberation of oxygen atom from a single crystal of V_2O_5 . From all these discussions, it emerges that vanadium pentoxide catalyst is a nonstoichiometric oxide having a certain degree of anion deficiency and hence a number of vacant anion sites with trapped electron pairs. Although there have been some studies on the changes of electrical conductivity of vanadium pentoxide with oxygen chemisorption, notably by Clark and Berets (7) and by Ioffe and Patrino (8), in order to ascertain the role of these quasi-free electrons in oxygen chemisorption and the nature of chemisorption bond, until now no work has been reported on the kinetics

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of chemisorption of oxygen on vanadium pentoxide.

Taylor and Thon (9), and also Low (10), have shown that the Elovich equation:

$$\frac{dq}{dt} = ae^{-\alpha q} \quad (1)$$

where q is the amount adsorbed, and a and α are constants denoting the initial rate and the deceleration of the process respectively, describes well adsorption on a large number of catalysts. In practice, it has been found that the slow process of chemisorption is often preceded by a very fast process. The recent important contribution of Cimino *et al.* (11) involves the modification of the integrated form of the Elovich equation as follows:

$$q = \frac{2.303}{\alpha} \log(t + t_0) - \frac{2.303}{\alpha} \log t_0 + q_0 \quad (2)$$

where q_0 is the amount adsorbed instantaneously before the slow process sets in, t_0 is an arbitrary constant and the other terms have their usual significance. These authors have also given new physical significance to the Elovich parameters in terms of the lifetime of "active sites" and proposed a model for the generation and decay of these "active sites."

EXPERIMENTAL

Preparation of the Catalysts (12)

Catalyst I. Vanadyl oxalate was prepared by adding the stoichiometric quantity of purified ammonium metavanadate (A.R.) to a solution of oxalic acid (A.R.) with stirring. The solution was dried on a water-bath with continuous stirring and the dried mass was further heated for 4 hr at a temperature of 120°C. This vanadyl oxalate was heated at 400°C for 4 hr in a continuous stream of air to give catalyst I.

Catalyst II. This catalyst was prepared by the thermal decomposition of ammonium metavanadate (A.R.) at a temperature of 400°C in a continuous stream of air for 4 hr.

Characterisation of the Catalysts

(i) Chemical analysis: The total V⁴⁺ and V⁵⁺ contents of both the catalysts were estimated by the standard methods of titration with potassium permanganate in acidic medium followed by reduction with sulphurous acid and a gain titration with permanganate.

(ii) Magnetic susceptibility measurements: Magnetic susceptibility of both the catalysts (I and II) were measured by the Gouy method with a magnetic balance at a field strength of 5.05×10^3 G.

(iii) Surface area measurements: These were made using nitrogen in a conventional BET unit.

Kinetics of Chemisorption Measurements

The measurements were carried out in a conventional volumetric adsorption apparatus by the constant volume method, where the drop in pressure (ΔP) is proportional to the volume adsorbed, in the temperature range 120–400°C with 20 g of each catalyst at an initial pressure of 20 cm of oxygen. Oxygen gas, formed by the decomposition of carefully degassed A.R. potassium permanganate crystals, was passed over anhydrous magnesium perchlorate.

Electrical Conductivity Measurements

The resistance of a pelleted sample was measured in the temperature range 100–480°C by a dc voltmeter, details of the methods and procedure being already given in an earlier paper (13).

The degassing before each experiment was carried out at 520°C for 8 hr following the procedure outlined in a previous paper (13).

RESULTS AND DISCUSSIONS

The physical characteristics of the two catalysts are given in Table 1. It is evident from Table 1 that, catalyst I has a larger concentration of V⁴⁺ ions than catalyst II. EPR measurements on the catalysts were made by Dr. H. M. E. Steiner at the Chemistry Department of the University of Manchester Institute of Science and Technology, who observed that the EPR signal

TABLE 1
PHYSICAL CHARACTERISTICS OF THE VANADIUM PENTOXIDE CATALYSTS

Catalyst	Prepared from	Surface area (m ² /g)	Magnetic susceptibility/g (emu)	V ⁴⁺ % (from chemical analysis)
I	Vanadyl oxalate	10.0	7.3×10^{-7}	2
II	Ammonium metavanadate	8.5	3.8×10^{-7}	1

for catalyst I is much stronger at $g = 2$ than that for catalyst II, indicating that the spin concentration due to presence of V⁴⁺ ions is considerably larger in catalyst I than catalyst II. In addition to the presence of V⁴⁺ ions at $g = 2$ lower valent

vanadium ions are indicated by an additional signal at $g = 4$.

The studies on the kinetics of chemisorption of oxygen on both the catalysts were made at 120, 250, 310, 360, and 400°C. ΔP is plotted against time in Fig. 1. It has

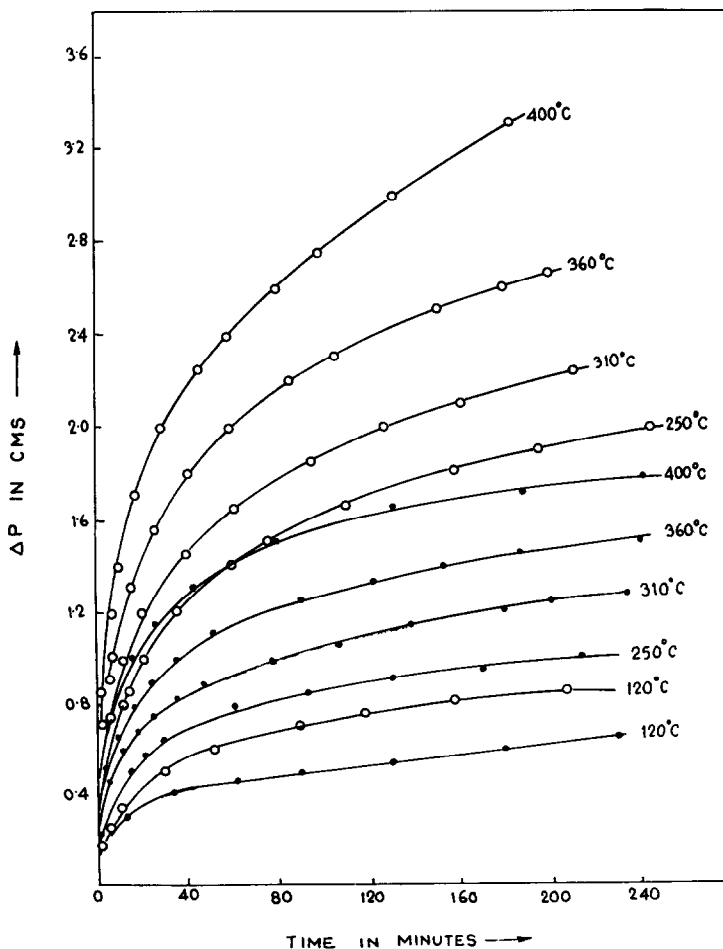


FIG. 1. Kinetics of oxygen chemisorption on vanadium pentoxide catalysts.

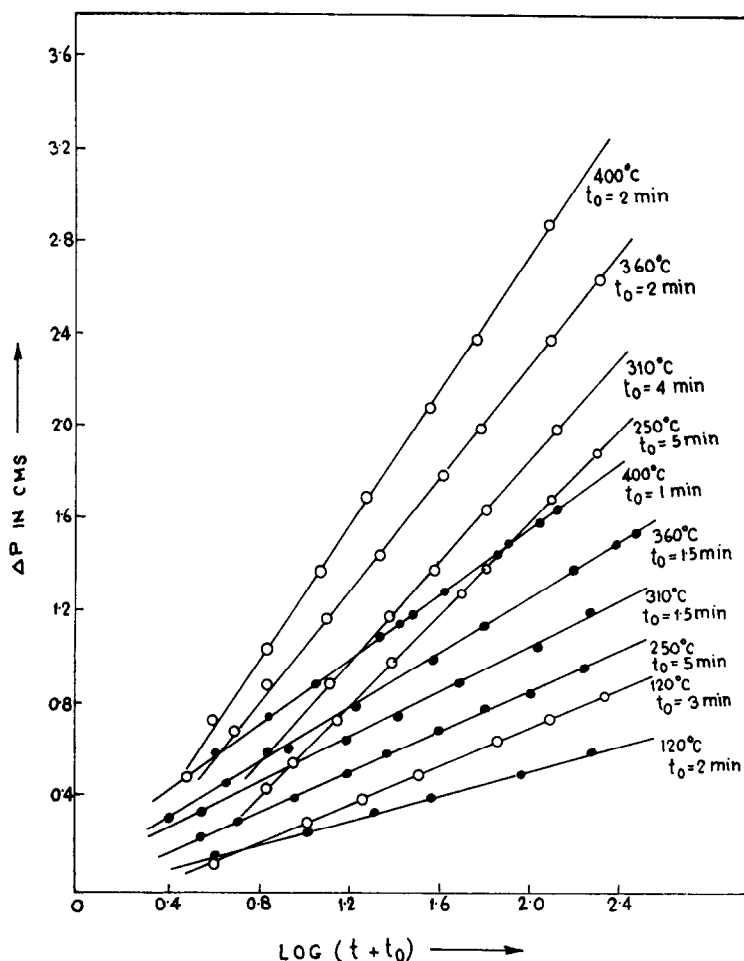


FIG. 2. Elovich plots for oxygen chemisorption on vanadium pentoxide catalysts.

been observed that in the temperature range 120–400°C up to 180 min the kinetics can be well described by the Elovich equation (2). The plots of Δp vs $\log (t + t_0)$ are

shown in Fig. 2 and the values of Elovich parameters are tabulated in Table 2.

The values of Δp and $1/\alpha$ for catalyst I were almost double the corresponding values

TABLE 2
ELOVICH CONSTANTS FOR OXYGEN ADSORPTION ON VANADIUM PENTOXIDE CATALYSTS

Temp. °C	Catalyst I				Catalyst II			
	α (cm ⁻¹ g)	$a \times 10^3$ (cm g ⁻¹ min ⁻¹)	$q_0 \times 10^3$ (cm g ⁻¹)	t_0 (min)	α (cm ⁻¹ g)	$a \times 10^3$ (cm g ⁻¹ min ⁻¹)	$q_0 \times 10^3$ (cm g ⁻¹)	t_0 (min)
120	108.70	3.01	3.49	3.0	168.4	2.97	2.74	2.0
250	46.06	4.34	14.95	5.0	104.6	6.37	2.88	1.5
310	41.88	5.10	16.11	4.0	92.0	7.23	7.40	1.5
360	37.86	13.21	9.76	2.0	80.0	8.33	10.56	1.5
400	31.64	23.10	18.22	2.0	65.2	15.30	7.75	1.0

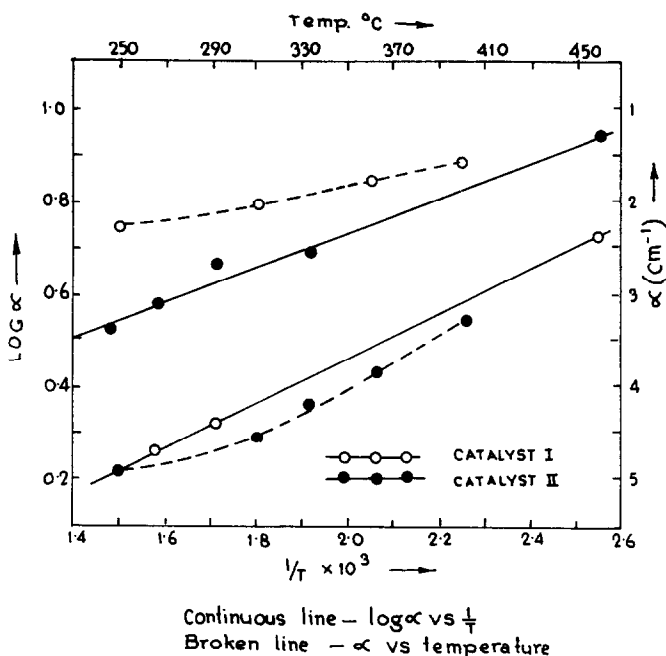


FIG. 3. Temperature dependence of α during oxygen chemisorption.

for catalyst II, at any particular temperature and initial pressure. Figure 3 shows the variation of the rate parameter α with temperature during oxygen chemisorption on both catalysts. From Fig. 3 a temperature coefficient of only about -2.28 kcal/mole is calculated from the plots of $\log \alpha$ vs $1/T$ for catalyst I while the corresponding value for catalyst II is only about -1.83 kcal/mole. The values of activation energy of oxygen chemisorption at different surface coverage are tabulated in Table 3.

The variations of log conductivity with reciprocal temperature for both the cata-

lysts under vacuum are shown in Fig. 4. Figure 5 represents the conductivity isobars, i.e., $-\Delta C/C\%$ (percentage decrease in conductivity) vs temperature in $^{\circ}\text{C}$ at 10 cms pressure of oxygen, while Fig. 6 shows the log-log plots of resistance against oxygen pressures at different temperatures.

Important differences in chemisorption of oxygen and the subsequent changes in the electrical conductivity can be summed up as follows:

(1) Although a decrease in the value of α with increasing temperature can be noticed in case of both the catalysts I and II, the value of α for catalyst I is much less than the corresponding value of α for catalyst II (Table 2).

(2) The other constants in the Elovich equation, a and q_0 , are found to increase progressively with increasing temperature. But for the same value of t_0 at a certain temperature the value of a is found to be greater for catalyst I than for catalyst II. Moreover, that the slow process of chemisorption is preceded by a very fast process of different kinetics is evident from the nonzero value of q_0 .

TABLE 3
ACTIVATION ENERGY FOR OXYGEN
CHEMISORPTION ON VANADIUM PENTOXIDE
CATALYSTS IN THE TEMPERATURE
RANGE 310–360 $^{\circ}\text{C}$

$\Delta P(\text{cm})$	E (Kcal/mole)	
	Catalyst I	Catalyst II
0.6	6.4	6.8
0.8	7.0	8.2
1.2	9.0	15.5

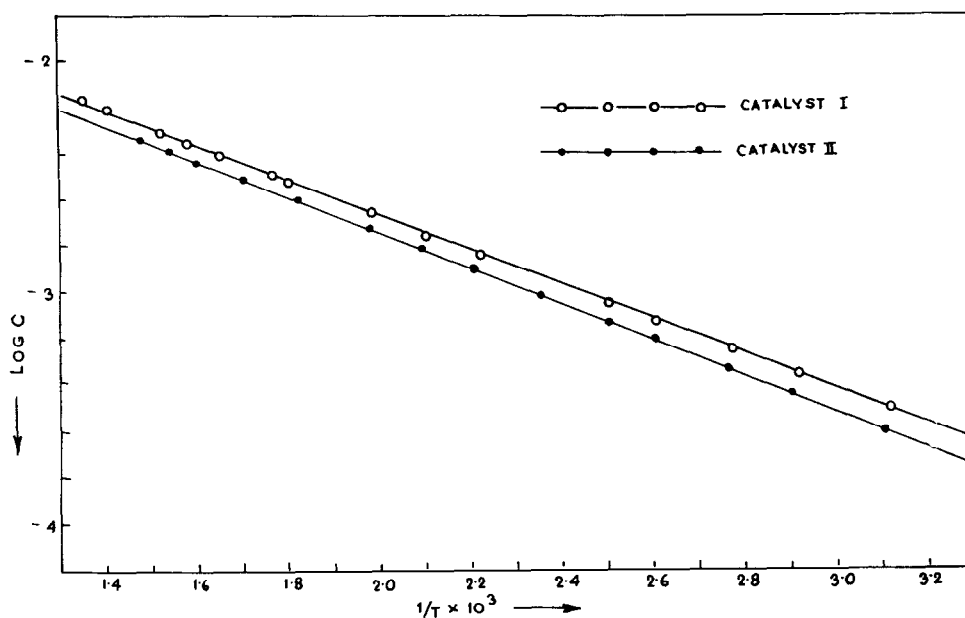


FIG. 4. Log conductivity vs reciprocal temperature under vacuum.

(3) The activation energy of oxygen chemisorption (Table 3) increases progressively with surface coverage. But for the same surface coverage, the value increases at a much faster rate for catalyst II. As this increase in activation energy is related

with the surface barrier effect (14) during chemisorption, one may suggest that in case of catalyst II the surface barrier is built up at a faster rate than in case of catalyst I.

(4) The conductivity isobars (Fig. 5)

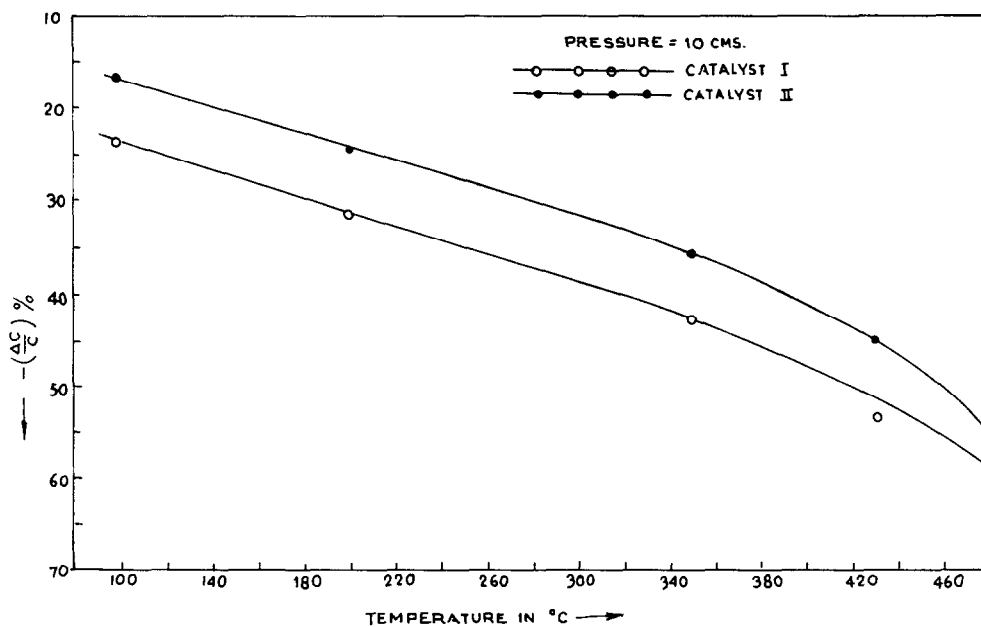


FIG. 5. Conductivity isobars for oxygen chemisorption on vanadium pentoxide catalysts.

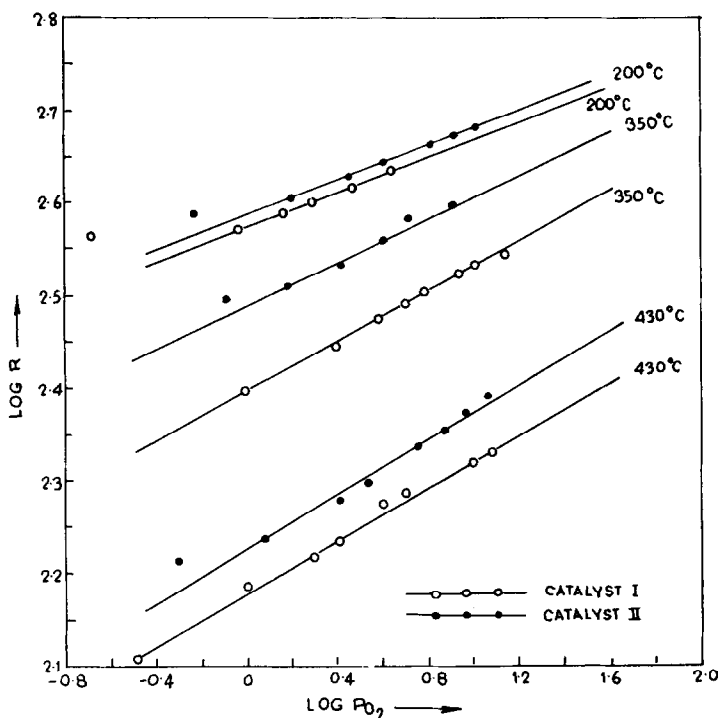


FIG. 6. Log-log plots of resistance vs oxygen pressure.

reveal that at any temperature and at all pressures the percentage decrease of conductivity ($-\Delta C/C\%$) is greater for catalyst I. This is compatible with the greater amount of oxygen chemisorbed by catalyst I under a given condition of temperature and pressure, since $-\Delta C/C\%$ is roughly proportional to the amount of oxygen chemisorbed.

(5) The activation energy for electrical conduction under vacuum, as found from the slope of the log conductivity vs reciprocal temperature plots (Fig. 4) is 0.17eV for catalyst I and 0.20eV for catalyst II. Thus it can be said that electrical conduction is easier for catalyst I than for catalyst II.

These differences in the behaviour of the two catalysts can be explained on the basis of a proposed model for the vanadium pentoxide surface.

Vanadium pentoxide, which is an *n*-type semiconductor, has quasi-free electrons and the anionic chemisorption of oxygen results in a decrease of electrical conductivity, as reported earlier by Clark and Berets (7)

and by Ioffe and Patrina (8). Adsorption of appreciable amounts of oxygen will result in the formation of a barrier layer preventing further adsorption. The rate of the chemisorption as well as the total amount chemisorbed will be dependent on the concentration of quasi-free electrons present in the lattice of vanadium pentoxide. Thus the increased rate and amount of oxygen chemisorption, as noticed in case of catalyst I, may be due to the presence of a greater concentration of quasi-free electrons in its lattice.

In the vanadium pentoxide lattice, anion vacancies with trapped electrons act as defect centres for conduction (15). However, the electrical properties of this compound have been sought to be closely dependent on the amount of V^{4+} ions present in its lattice (4, 5, 8). Gillis and Boesman (16) have concluded from the studies on the EPR spectra of vanadium pentoxide single crystals that a defect centre consists of an unpaired electron interacting with two equivalent vanadium nuclei separated by an oxygen vacancy. They have also sug-

gested that one of the vanadium nuclei may be a V^{4+} ion. Thus V^{4+} ions are always associated with oxygen vacancies in vanadium pentoxide lattice.

It is evident from the results of chemical analysis and magnetic susceptibility measurements (Table I) that catalyst I has greater concentration of V^{4+} ions and hence greater concentration of unpaired electrons and anion vacancies in its crystal lattice compared to catalyst II. The greater concentration of the electrons and anion vacancies in the lattice of catalyst I accounts for the increased rate and amounts of chemisorption in comparison with catalyst II.

Oxygen may be chemisorbed on the vanadium pentoxide surface either as O_2^- , O^- , or O^{2-} depending upon the availability of electrons and energy requirements of the surface. Whatever the nature of chemisorbed oxygen on the surface of vanadium pentoxide may be, the linear nature of the $\log \alpha$ vs $1/T$ plots (Fig. 3) for both the catalysts shows that at temperatures from 120–400°C only one form of oxygen chemisorption bond may be formed on the surface of vanadium pentoxide lattice, irrespective of the methods of preparation (11). It may be argued, however, that the same type of oxygen chemisorption bond may not be formed on the surface of the two vanadium pentoxide catalysts. But in case of vanadium pentoxide catalysts (I and II) the fact that the same species of chemisorbed oxygen may be formed is evident from the similar nature of Elovich plots (Figs. 2 and 3). Moreover, the log-log plots of resistance against oxygen pressure have almost the same slope in the temperature range 100–480°C for both the catalysts, as observed by Clark and Berets (7), indicating that the concentration of carriers varies with oxygen pressure in the same way in case of catalyst I as in case of catalyst II. This implies that whatever may be the nature of the chemisorbed oxygen species, O_2^- , O^- , or O^{2-} , only one type of chemisorption bond is involved and the nature of the chemisorption bond is always the same in case of both catalysts.

From isotopic exchange studies of oxygen

on vanadium pentoxide in the temperature range 400–550°C by Cameron and Farkas (17), it is seen that oxygen can dissociate on the surface at these temperatures. Since there is no essential difference between the nature of the chemisorption data below 400°C with those at 400°C, we may further say that dissociative chemisorption of oxygen takes place at all temperatures ranging from 100–480°C. Moreover, if oxygen becomes chemisorbed as O_2^- , the resistance is expected to vary directly as the oxygen pressure, according to the equation $O_2(g) + e \rightarrow O_2^-(ads)$. In fact, such a dependence has not been observed by the authors (Fig. 6). The resistance shows nearly fourth root dependence with oxygen pressure, which indicates that oxygen is being adsorbed as O^{2-} , most probably according to the mechanism proposed by Clark and Berets (7).

SUMMARY

Catalyst I, prepared by the thermal decomposition of vanadyl oxalate, has been characterised as having greater surface area, higher magnetic susceptibility and larger concentration of V^{4+} ions than catalyst II, prepared by the decomposition of ammonium metavanadate. The kinetics of chemisorption of oxygen between 120–400°C obeys the Elovich equation in both cases. No discontinuity is marked in the plots of the Elovich constant, α , with temperature. Thus it is suggested that one type of oxygen chemisorption bond is formed on the surface of both the catalysts.

The rate of chemisorption and the extent of the percentage decrease in electrical conductivity during oxygen chemisorption are found to be greater for catalyst I. The activation energy for oxygen chemisorption is found to increase with surface coverage in both cases, but the increase is much faster in case of catalyst II. It has been suggested that the increased activity for oxygen chemisorption, as noticed in case of catalyst I, may be due to the presence of a greater concentration of anion vacancies and quasi-free electrons in its crystal lattice. The probability of the formation of

O²⁻ ions as the chemisorbed species has also been discussed.

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