KINETICS OF CHEMISORPTION OF HYDROGEN, OXYGEN AND CARBON MONOXIDE ON VANADIUM PENTOXIDE

by KALYAN SASI DE *and* (MRS.) K. GADGIL*, *Department of Chemistry,*
Indian Institute of Technology, Kharagpur, West Bengal

Kinetic studies on the chemisorption of different gases on vanadium pentoxide, prepared by the thermal decomposition of ammonium meta vanadate at 400°C in presence of air, have been made. The catalyst has been characterised by chemical analysis, surface area determination, X-ray diffraction pattern, I.R. Spectra, magnetic susceptibility measurement and differential thermal analysis.

Kinetics of chemisorption of hydrogen on V_2O_5 and of H_2, CO and O_2 on differently treated V_2O_5 have been studied in the temperature range 275°—350°C at an initial pressure of 8.8 cm of Hg. Elovich equation has been found to be obeyed. Activation energies for the chemisorption of hydrogen, when calculated by different methods, show reasonably good agreement. The results have been interpreted in terms of O^- or O^{--}, H_2^+, H^+, OH^- surface species and lower valent states of vanadium. A probable mechanism of chemisorption has been suggested.

INTRODUCTION

Research in heterogeneous catalysis has greatly advanced during recent years. The elucidation of the nature of catalysts by physisorption and chemisorption studies has proved to be of immense value in predicting catalytic behaviour of solid catalysts (cf. Roberts & Wells 1966; Temkin & Kul'kova 1955; Hirota & Kobyashi 1956; and Peshev 1966).

Among the oxidation catalysts, vanadium pentoxide has found extensive use in many industrial processes. However, irrespective of its method of preparation and purity, V_2O_5 is invariably associated with about 1 per cent V^{4+} (and possibly other lower valent states). Vol'fson *et al.* (1965) detected the presence of at least nine phases of composition V_nO_{2n-1} (n = 2—7), V_nO_{2n}(n=2), V_nO_{2n+1} (n=2, 6) between V_2O_3 and V_2O_5. It has been shown that the presence of lower valent states either singly or in combination with V_2O_5 is responsible for the catalytic activity of the oxide (Simard *et al.* 1955).

Mars and van Krevelen (1954) have expressed the view, that the crystal chemistry of V_2O_5 may play a part in the adsorption reactions involving V_2O_5. It has also been shown that a depletive chemisorption occurs in the case of adsorption of oxygen on V_2O_5 (cf. Ioffe & Patrina 1964). However, the upto-date investigations on the physicochemical properties of V_2O_5 has been rather fragmentary, so that an understanding of the adsorptive and catalytic characteristics of the oxide still remain a complicated problem.

Present Address : Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi-110029.

The present investigation deals with some aspects of this problem through a study of kinetics of chemisorption of H_2, CO and O_2 on differently treated V_2O_5.

<div align="center">EXPERIMENTAL</div>

Preparation and Characterisation of V_2O_5 : The V_2O_5 sample was prepared by the thermal decomposition of ammonium-meta-vanadate (Riedel) at $400°C \pm 1°C$ in presence of air. The sample thus prepared was powdered, sieved and the specimen between -120 and $+140$ B.S.S. was chosen for chemisorption studies.

The prepared V_2O_5 was chemically analysed by the method of Caderbank (1952) and the percentage of V^{4+} was found to be 1.1.

X-ray diffraction patterns were obtained using a 28.65 mm diameter camera (Philips Model P. W. 1008) and chromium radiation ($\lambda = 2.291\overset{\circ}{A}$). The 'd' values agreed with standard patterns of V_2O_5.

The magnetic susceptiblity measurements were carried out before and after adsorption, using a Gouy balance. The differential thermal analysis was done on a manually operated instrument.

The surface area of the oxide sample was determined by the BET method using N_2 as the adsorbate at liquid air temperature both before and after adsorption. The values were 10.1 m^2/g (before adsorption) and 5.1 m^2/g (after adsorption).

Preparation of Gases : Oxygen was prepared by the thermal decomposition of $KMnO_4$ (AR) and was collected over di-*n*-butyl phthalate after drying over P_2O_5.

Hydrogen supplied by M/s. Indian Oxygen Ltd., Calcutta, was purified by passing through hot copper gauze at $400°C$, heated platinized asbestos and finally through silica-gel kept at liquid air temperature.

Carbon monoxide was prepared by adding formic acid drop by drop to hot concentrated sulphuric acid (analar). The gas thus obtained was purified by the usual methods and finally analysed in an Orsat apparatus. The purity was found to be 99.4 per cent.

Adsorption Studies : A conventional BET apparatus was used for adsorption measurements. About 1.0 g sample of V_2O_5 was taken and degassing and evacuation was done at $430°C$ for 4 hours. Kinetic measurements were carried out at constant volume in the temperature range $275°$ to $350°C$. Each time a constant volume of the gas was introduced and the resulting change in pressure ($\triangle p$) was noted. The amount of gas adsorbed (q), was found to be proportional to the change in pressure ($\triangle p$). Rates became appreciable around $275°C$. Elovich equation was found to be obeyed, which was tried in the following form given by Low (1960) :

$$\triangle p = \frac{2.303}{\alpha} \log (t + k) + \text{const.} \qquad .. \qquad .. \qquad .. \quad (I)$$

where $t =$ time (in minutes), and α and k are constants, such that

$\dfrac{1}{\alpha\,t} =$ rate of initial rapid adsorption (a),

$\dfrac{1}{\alpha\,k} =$ rate of initial adsorption provided the initial rapid adsorption is without

effect on the succeeding slow adsorption (a*),

and $\dfrac{1}{\alpha\,(t + k)} =$ rate of overall adsorption.

The experiments were carried out in the following sequence :

   (*i*) Adsorption of hydrogen at 275°, 300°, 325° and 350°C (Expts Nos. 1–4).

   (*ii*) Adsorption of carbon monoxide at 275° and 300°C. (Expts Nos. 5 and 6).

   (*iii*) Adsorption of hydrogen at 300°C (Expt. No. 7).

   (*iv*) Adsorption of oxygen at 300°C (Expt. No. 8).

and (*v*) Adsorption of hydrogen at 300°C (Expt. No. 9).

RESULTS AND DISCUSSIONS

The results of the kinetics of hydrogen adsorption obtained at 275°, 300°, 325° and 350°C are shown in Table I and the corresponding Elovich parameters are given in Table II. It is seen that the initial rate of adsorption (a) increased between 275° and 325°C and decreased at 350°C while the overall rate (as reflected in decreasing α values) increased in the range 275° to 350°C although the amount of chemisorbed hydrogen at 350°C was slightly less than that at 325°C.

The plots of $\triangle p$ *vs.* log *t* (Fig. 1a) are linear but discontinuous. There are two breaks in each plot. The plots for the experimental runs at 300°, 325° and 350°C could be linearised by choosing a suitable value of 'k' (Fig. 1b). However, the plot at 275°C could not be completely linearised.

TABLE I

Adsorption of hydrogen on V$_2$O$_5$

Expt. No. 1 $p = 8.8$ cms $t = 275°C$		*Expt. No.* 2 $p = 8.8$ cms $t = 300°C$		*Expt. No.* 3 $p = 8.8$ cms $t = 325°C$		*Expt. No.* 4 $p = 8.8$ cms $t = 350°C$	
Time (min)	$\triangle p$ (cm. of Hg)	Time (min)	$\triangle p$ (cm. of Hg)	Time (min)	$\triangle p$ (cm. of Hg)	Time (min)	$\triangle p$ (cm. of Hg)
1	0.12	1	0.22	1	0.62	1	0.20
2	0.13	2	0.23	2	0.68	2	0.22
4	0.13	4	0.24	4	0.73	4	0.27
6	0.13	6	0.25	6	0.80	6	0.36
8	0.14	8	0.27	8	0.85	8	0.42
10	0.15	10	0.29	10	0.90	10	0.47
15	0.17	15	0.31	15	0.92	15	0.58
20	0.20	20	0.35	20	1.10	20·	0.62
25	0.25	25	0.38	25	1.13	25	0.70
30	0.27	30	0.41	30	1.20	30	0.80
40	0.35	40	0.44	40	1.30	40	0.88
50	0.37	50	0.45	50	1.35	50	0.93
60	0.40	60	0.47	60	1.37	60	1.00
75	0.42	75	0.51	75	1.50	75	1.18
90	0.45	90	0.54	90	1.52	90	1.34
105	0.51	105	0.57	105	1.59	105	1.42
120	0.52	120	0.60	120	1.60	120	1.50

TABLE II

Elovich parameters for the Adsorption of Hydrogen on V_2O_5

$p = 8.8$ cms

Temp. °C	α (cm^{-1} gm)	$\triangle p_0$ (cm)	t_0 (min)	k (min)	a (cm. gm min^{-1})	a_1 (cm. gm. min^{-1})	a_2 (cm. gm. (min^{-1}))	$\log a_3$
275	22.14	0.12	0.57	9	0.1052	0.00502	0.0001512	—5.2413
300	6.97	0.20	2.50	10	0.15285	0.014	0.00248	—3.3670
325	2.71	0.61	1.70	9	0.2130	0.041	0.007874	—2.8199
350	1.87	0.19	10.50	15	0.05076	0.0355	0.02494	—1.7574
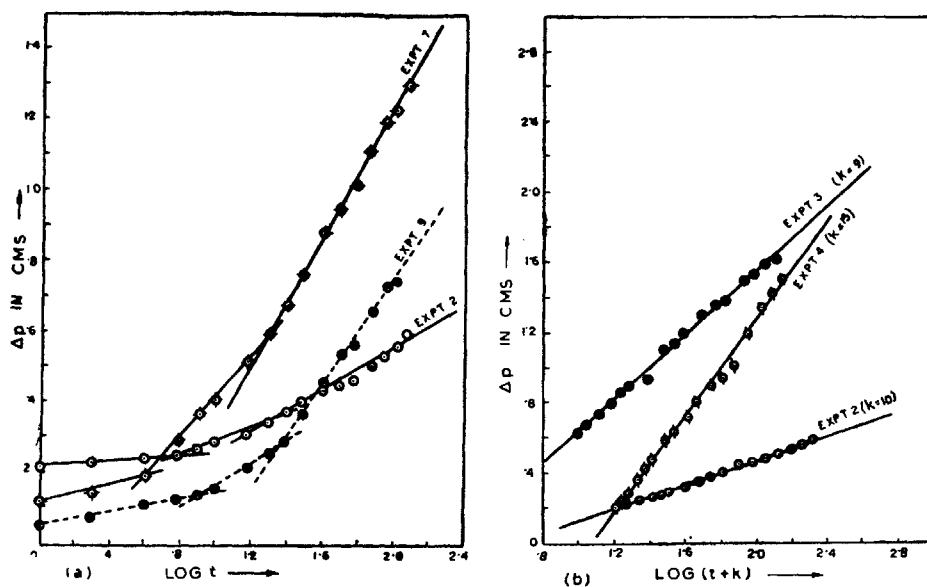
FIG. 1.   Elovich plots for hydrogen chemisorption on V_2O_5

The values of α were determined from the plots of $\triangle p$ vs. $\log (t + k)$. The plot of α vs. $\frac{1}{T}$ (Fig. 2a) is continuous without any maxima or minima of the kind observed by Ogden and Taylor (1934) and Shastri and Ramanathan (1952) suggesting thereby that probably no major change in active sites are involved in the overall chemisorption process in the temperature range studied.

The results of adsorption of carbon monoxide on the surface on which hydrogen adsorption has been carried out indicated a very low rate.

Adsorption of hydrogen on the surface on which carbon monoxide adsorption has been carried out is characterised by a much higher rate and the amount adsorbed in 120 minutes also increased (Table III).   The chemisorption of oxygen over such a
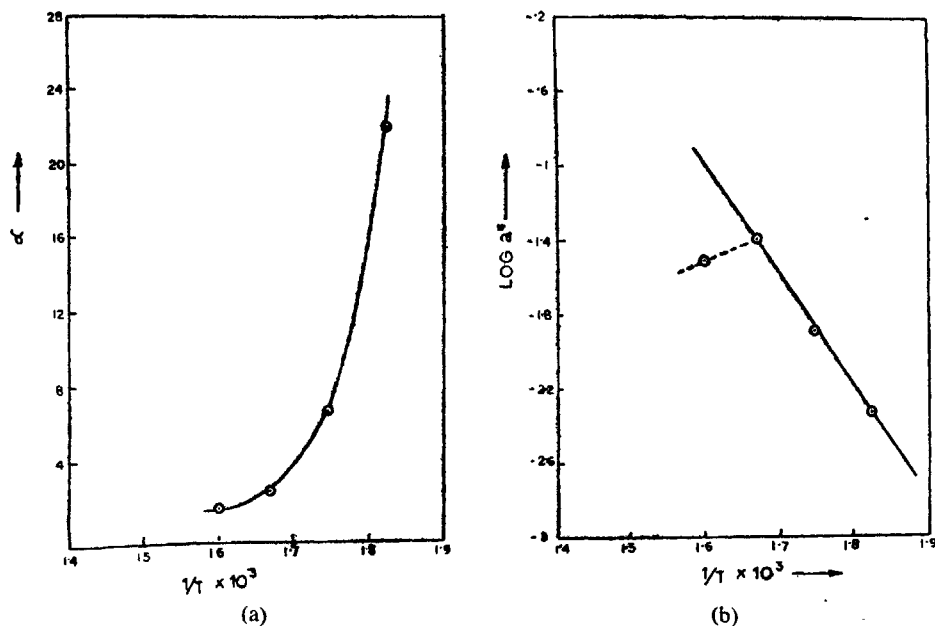
FIG. 2 (a). Plot of α vs. $1/T$; (b). Plot of log a^* vs. $1/T$

TABLE III

Adsorption of H_2, O_2 and H_2 on surface treated with (a) CO, (b) CO and H_2 and (c) O_2, respectively.

(a)		(b)		(c)	
Expt. No. 7		*Expt. No. 8*		*Expt. No. 9*	
$P = 8.80$ cms		$P = 8.80$ cms		$P = 8.80$ cms	
$t = 300°C$		$t = 300°C$		$t = 300°C$	
Time (min)	$\triangle p$ (cm. of Hg)	Time (min)	$\triangle p$ (cm. of Hg)	Time (min)	$\triangle p$ (cm. of Hg)
1	0.12	1	0.08	1	0.05
2	0.14	2	0.09	2	0.07
4	0.20	4	0.11	4	0.11
6	0.30	6	0.12	6	0.13
8	0.37	8	0.13	8	0.14
10	0.40	10	0.14	10	0.15
15	0.52	15	0.17	15	0.22
20	0.60	20	0.18	20	0.26
25	0.68	25	0.19	25	0.29
30	0.77			30	0.37
40	0.88			40	0.46
50	0.95			50	0.54
60	1.02			60	0.57
75	1.12			75	0.66
90	1.20			90	0.73
105	1.23			105	0.74
120	1.30				

surface proceeds at a slow rate as can be seen from Table III. Comparison of these results with those of Bhattacharyya and Mohanty (1968) shows that no conducive sites for O_2 adsorption have been created as a result of H_2 and CO adsorption on V_2O_5 at these temperatures. Oxygen adsorption on the surface of V_2O_5 however, has appreciable effect on the subsequent H_2 adsorption on it (Table III).

Activation energy for the adsorption of hydrogen, calculated from the plot of $\log a^*$ vs. $\frac{1}{T}$ (Fig. 2b), gave a value of 27.4 kcal/mole in the temperature range 275° to 325°C, while a negative value was indicated in the temperature range 325°—350°C. Such behaviour has also been observed by Cimino et al. (1960); and Shershefsky and Russel (1956); who have tried to attribute this to the occurrence of two distinct processes, one increasing and the other decreasing, with temperature. But then, the activation energy, be it positive or negative, is of little mechanistic significance. To obviate this and for a better appreciation of the kinetics of chemisorption, the procedure of Allen and Scaiffe (1966) has been followed. In this procedure the kinetic data are fitted to the equation of the form :

$$\frac{d\triangle p}{dt} = a_\gamma \exp\left\{- \alpha (\triangle p - \gamma \triangle p_o)\right\} \qquad \qquad \qquad (2)$$

where $\triangle p_i$ is the amount adsorbed at $t = 0$ and γ is a constant, so that a_γ is related to a^* by

$$a_\gamma = a^* \exp\left\{-(\gamma - 1) \alpha \triangle p_o\right\} \qquad \qquad \qquad (3)$$

whence a^* is a_1.

In the present case, $\triangle p_o$, t_o and a_2, a_3 etc. have been calculated by the following equations :

$$\triangle p_t = \frac{2.303}{\alpha} \log (t+k) - \frac{2.303}{\alpha} \log t_o \qquad \qquad \qquad (4)$$

$$k = t_o \exp(\alpha\triangle p_o) \qquad \qquad \qquad (5)$$

$$\triangle p_o = \frac{2.303}{\alpha} \log \left(\frac{k}{t_o} \right) \qquad \qquad \qquad (6)$$

and $$a_2 = a_1 e^{-1\alpha \triangle p_o} \qquad \qquad \qquad (7)$$

$$a_3 = p_1 e^{-2\alpha \triangle p_o} \qquad \qquad \qquad (8)$$

The plots of $\log a_2$ $\log a_3$ and $\log a_4$ vs. $\frac{1}{T}$ (Fig. 3a and 3b) are all continuous and the activation energies determined are positive with values 33.95, 70.7 and 106.8 kcals/mole respectively.

The results of activation energy thus calculated support that the most suitable value of γ is 2; for the value of the activation energy of the order of $\sim$ 34 kcal/mole is most likely compared to the higher values.

Activation energy has also been calculated by the use of the equation

$$\log (rate) = \log\left(\frac{d\triangle p}{dt}\right) = \log a - \frac{\alpha}{2.303} \triangle p_o \qquad \qquad \qquad (9)$$
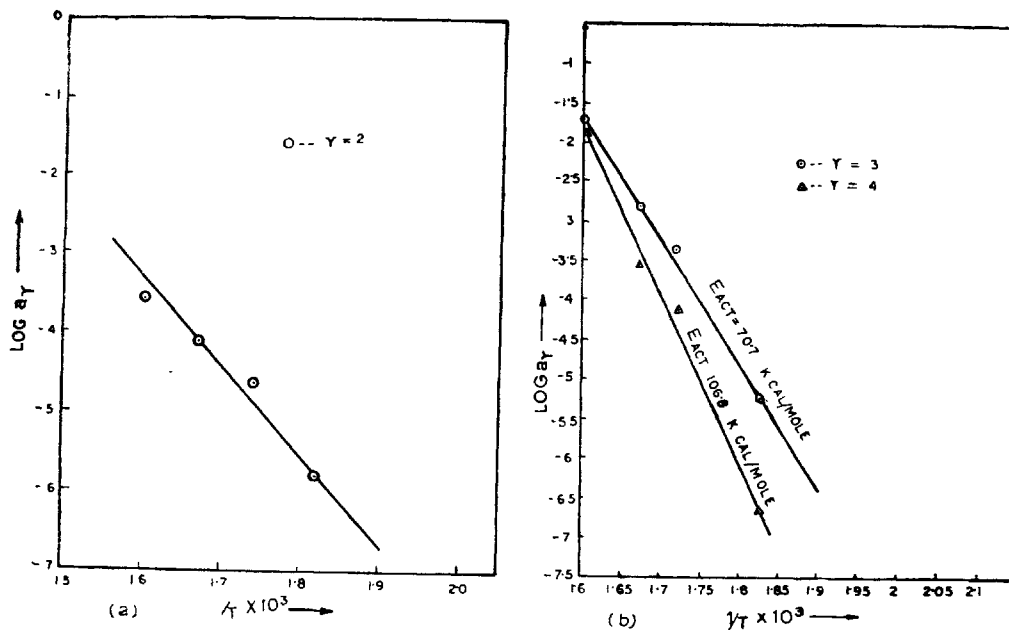
FIG 3.   Plots of log a_γ vs. $1/T$ for hydrogen chemisorption on V_2O_5 For (a), $E_{ACT}=33.95$ K cal/Mole.

and the value has been found to be almost the same. The equation was tried with both a_1 and a_2 and in both cases the results were quite regular. Activation energy was found to increase linearly with coverage, the relations from the plots (Figs. 3a and 3b) for a_1 and a_2 being :

$$E_{\Delta p} = 100_{\Delta p} + 33, \text{ and } E_{\Delta p} = 60_{\Delta p} + 36.9 \ (\pm \ 0.2) \text{ respectively.}$$

The value for zero coverage was better reproduced in the case where a_2 was used. This also support that the probable value for γ is equal to 2 for the system under investigation.

There is no adsorption of hydrogen upto 275°C indicating the activation energy to be very high. The kinetic energy of hydrogen may not be sufficient to cross the activation barrier for adsorption below this temperature.

From the study of EPR spectra of V_2O_5, recently, Gillis and Boesmann (1966) showed that defect centres (d_1), consisting of an unpaired electron interacting with two equivalent vanadium nuclei separated by an oxygen vacancy, may be present in V_2O_5. They also suggested that one of the two vanadium nuclei may be V^{4+} ion. So the energy level diagram of V_2O_5 must contain such levels apart from the lattice vacancies O_v^{--} and O_v^{-} as suggested by Clark and Berets (1957).

The experimentally obtained high activation energy values probably indicate the adsorption at 'd_1' level to be rate determining, at least during the initial stages, because the activation energy should not be so high for adsorption via O_v^{--} or O_v^{-} vacancies. From electrical work function measurement, hydrogen has been shown to be adsorbed on V_2O_5 as a donor giving its electron to the bulk semiconductor (cf. Enikeev et al. 1959). On this basis, adsorption at 'd_1' level may be represented as :

$$H_2 + \square_s^+ \longrightarrow H_2^+ \diagup \square_s^+ + e \qquad \qquad .. \qquad .. \qquad .. \quad (10)$$

At high temperatures, H_2^+ will not be stable and will dissociate into H^+ and H according to the equation :

$$H_2^+ \diagup \square_s^+ \longrightarrow H^+ \diagup \square_s^+ + H \qquad \qquad .. \qquad .. \qquad .. \quad (11)$$
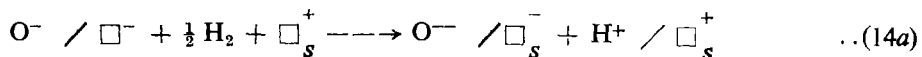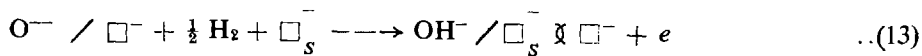
The energy required for the overall process is about 16.30 eV. However, if the adsorption takes place at the start by dissociation of hydrogen and then by ionisation of H, the energy required would be 18.3 eV., which is higher and is, therefore, less likely. So, it is believed that 'H' formed according to equation 11 forms a covalent bond with 'd$_1$' level, which can be represented following Rees (1954) notation as :

$$\left(e/2V^{5+} \diagup \square_s^+ \right) + H \longrightarrow \left(H2e/2V^{5+}/ \square_s^+ \right) \qquad \qquad .. \qquad .. \qquad .. \quad (12)$$
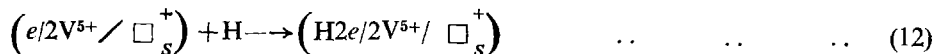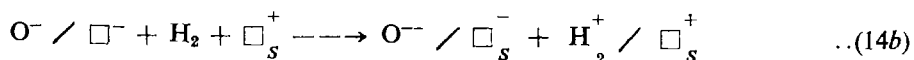
In the sequence of experiments, the concentration of 'd$_1$' is highest in experiment No. 2 and lowest in experiment No. 9. Therefore, the initial fast adsorption should be highest in experiment No. 2, if equation 12 is rate determining. This has been found to be the case (Tables I and III).

Adsorption in the later stages may take place via $O_v^{-\,-}$ and O^- levels through associated O^- or $O^{-\,-}$ species according to the following equations :

$$O^{-\,-} \diagup \square^- + \tfrac{1}{2} H_2 + \square_s^- \longrightarrow OH^- \diagup \square_s^- \text{ or } \square^- + e \qquad \qquad ..(13)$$

$$O^- \diagup \square^- + \tfrac{1}{2} H_2 + \square_s^+ \longrightarrow O^{-\,-} \diagup \square_s^- + H^+ \diagup \square_s^+ \qquad \qquad ..(14a)$$

or

$$O^- \diagup \square^- + H_2 + \square_s^+ \longrightarrow O^{-\,-} \diagup \square_s^- + H_2^+ \diagup \square_s^+ \qquad \qquad ..(14b)$$
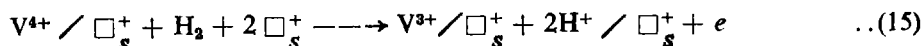
Consumption of $O^{-\,-}$, giving OH^- according to equation 13 is, however, unlikely according to Morrison (1955). At high temperatures H_2^+ will be unstable and therefore adsorption according to equation 14a is more probable compared to equation 14b. The $O^{-\,-}$ species formed (Equation 14a) may lose electrons to the conduction band immediately giving rise to O^- species for further adsorption (cf. Clark and Berets 1957). This promotion requires some energy and thus activation energy increases with coverage. Apparently, adsorption in this process may be unlimited. But the H^+ present in the surface may provide activation barrier for formation of further H^+ limiting the amount adsorbed to a low value, as observed at 350°C.
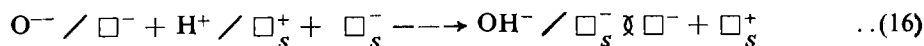
A surface on which oxygen adsorption has been carried out will naturally contain more O^- ions and the amount adsorbed will increase. A surface, on which carbon monoxide has been adsorbed, during outgassing leads to an even higher concentration of O^- thereby showing a very large increase in the amount of hydrogen adsorbed.

The V^{4+} nuclei present in V_2O_5 may be attacked by hydrogen giving rise to V^{3+} according to equation :

$$V^{4+} \diagup \underset{s}{\square^+} + H_2 + 2\underset{s}{\square^+} \longrightarrow V^{3+} \diagup \underset{s}{\square^+} + 2H^+ \diagup \underset{s}{\square^+} + e \qquad ..(15)$$
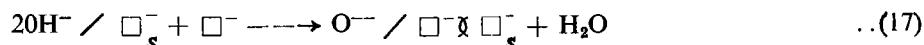
This reaction, which is also supported from thermodynamic view point (cf. Samytova et al. 1959) may be operative at higher temperatures leading to a higher rate as at 350°C. At lower temperatures, however, this will have no significant effect.

The reduction in surface area from 10.1 m²/g to 5.1 m²/g after hydrogen adsorption may be attritubed to the fact that at temperature very close to the Tamman temperature, the H^+ species present on the surface became mobile and may attack O^{--} forming OH^- as follows :

$$O^{--} \diagup \square^- + H^+ \diagup \underset{s}{\square^+} + \underset{s}{\square^-} \longrightarrow OH^- \diagup \underset{s}{\square^-} \, \mathfrak{g} \, \square^- + \underset{s}{\square^+} \qquad ..(16)$$

This may give rise to water :

$$2OH^- \diagup \underset{s}{\square^-} + \square^- \longrightarrow O^{--} \diagup \square^- \mathfrak{g} \, \underset{s}{\square^-} + H_2O \qquad ..(17)$$

thus flooding the lattice and reducing the surface area (cf. Cotton and Fensham 1963).

However, the adsorption of carbon monoxide and oxygen has not been studied in detail. Adsorbtion of carbon monoxide on 'd_1' level would give rise to CO^+. These CO^+ species, by attack on $O^{--} \diagup \underset{s}{\square^-}$ and $O^{--} \diagup$ $\square^-$, would create more and more O_v levels forming CO_2. These $\underset{v}{O^-}$ levels through their associated O^- species would facilitate more hydrogen adsorption on CO–preadsorbed V_2O_5 surface (Table III). Preadsorption of oxygen on the surface leading to formation of O^{--} and O^- as given by Barry and Stone (1960) will facilitate subsequent hydrogen adsorption.

The results, in general, tend to show that while the rate of overall hydrogen adsorption on untreated V_2O_5 increases with temperature (275°—350°C), that on a pretreated sample is markedly dependent on the nature of adsorbed gas (300°C).

REFERENCES

Allen, J. A., and Scaiffe, P. H. (1966). The Elovich equation and chemisorption kinetics. *Aust. J. Chem.*, 19, 2015–2023.

Barry, T. I., and Stone, F. S. (1960). The reactions of oxygen at dark and irradiated zinc oxide surfaces. *Proc. R. Soc.*, A255, 124–144.

Bhattacharyya, S. K., and Mohanty, P. (1968). Chemisorption and electrical conductivity studies on vanadium pentoxida catalysts. *Proc. IV Int. Congr. Catal.*, 1, 316–323.

Caderbank, P. H. (1952). The mechanism of catalytic oxidation of sulphur dioxide with a commercial vanadium catalyst : a kinetic study. *J. appl. Chem.*, 2, 482–492.

Cimino, A., Molinari, E., and Cipollini, E. (1960). On the mechanism of hydrogen chemisorption on zinc oxide semiconductors. *Actes Du Den. Congr. Int. de Catalyse.*, 2nd, (Paris), 1, 263–273.

Clark, H., and Berets, D. J. (1957). Vanadium oxides as oxidation catalysts : electrical properties. *Adv. Catal.*, **9**, 204–214.

Cotton, J. D., and Fensham, P. J. (1963). Depletive adsorption of hydrogen and Carbon Monoxide on nickel oxide. *Trans. Farad. Soc.*, **59**, 1444–1457.

Enikeev, E. Eh., Margolis, L. Ya., and Roginskii, S. L. (1959). Effect of the surface charge of ZnO on the rate of chemisorption of oxygen. *Dokl. Akad. Nauk. SSSR.*, **129**, 372–375.

Gillis, E., and Boesman, E. (1966). E. P. R. studies of V_2O_5 single crystals. I. Defect centres in pure nonstoichiometric V_2O_5. *Phys. Sol. State.*, **14**, 337–47.

Hirota, K., and Kobayashi, Y. (1956). Anomalous catalytic activity of reduced silver. *Bull. chem. Soc. Japan*, **29**, 996–998.

Ioffe, V. A., and Patrina, I. B. (1964). Electron paramagnetic resonance in V_2O_5 single crystals. *Fiz. Tverd. Tela.*, **6**, 3045–3049.

Low, M. J. D. (1960). Kinetics of chemisorption of gases on solids. *Chem. Rev.*, **60**, 267–312.

Mars, P., and van Krevelen, D. W. (1954). Oxidations carried out by means of vanadium oxide catalysts. *Chem. Engng. Sci.*, 3 (special supplement, Proc. of the conferences on oxide processes), 41–59.

Morrison, S. R. (1955). Surface barrier effects in adsorption illustrated by zinc oxide. *Adv. Catal.*, **7**, 259–301.

Ogden, G., and Taylor, H. S. (1934). The adsorption of hydrogen and of carbon monoxide on a surface of zinc and molybdenum oxides. *Trans. Farad. Soc.*, **30**, 1178–1190.

Pahari, S. S. (1963). Physico-chemical studies on catalysts : adsorption of gases on silver oxide. Ph. D. Thesis, Indian Institute of Technology, Kharagpur.

Peshev, O. (1966). The electronic factor in the kinetics of chemisorption on semiconductors. *Russ. chem. Revs.*, **35**, 761–772.

Rees, A. L. G. (1954). *Chemistry of the defect solid state.* Methuen and Co., London, 15–20.

Roberts, M. W., and Wells, B. R. (1966). Chemisorption and incorporation of oxygen by nickel films. *Trans. Farad. Soc.*, **62**, 1608–1619.

Samytova, S. T., Salivaeva, P. O., and Panonarev, V. D. (1959). Behaviour of vanadium oxides at high temperatures. *Chem. Abst.*, **70**, 81415.

Shastri, M. V. C., and Ramanathan, K. V. (1952). Chemisorption of hydrogen on zinc oxide-molybdenum oxide catalyst. Evidence of heterogeneity of the surface. *J. phys. Chem.*, **56**, 220–224.

Shershefsky, N. Y., and Russel, E. R. (1956). Active adsorption of oxygen on glass. *J. phys. Chem.*, **60**, 1164–1166.

Simard, G. L., Steger, J. F., Arnal, R. J., and Siegel, L. A. (1955). Vanadium oxides as oxidation catalysts. *Ind. Engng. Chem.*, **47**, 1424–1430.

Temkin, M. I., and Kul'kova, N. V. (1955). The nature of slow gas sorption by solids. *Dokl. Akad. Nauk. SSSR.*, **105**, 1021–1023.

Vol'fson, V. Ya., Zhigailo, Ya. V., Totskaya, E. F., and Raksha, V. V. (1965). Nature of the active component of a vanadium oxide catalyst for naphthalene oxidation. *Kinet. Katal.*, **6**, 162–166.