

## Adsorption Kinetics of O<sub>2</sub> on V<sub>2</sub>O<sub>5</sub>

N. E. QUARANTA, L. A. GAMBARO, AND H. J. THOMAS<sup>1</sup>

*Centro de Investigación y Desarrollo, en Procesos Catalíticos CINDECA, Calle 47 N° 257,  
1900 La Plata, Argentina*

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Oxygen chemisorption was measured on V<sub>2</sub>O<sub>5</sub> within the range of 473 to 723 K at O<sub>2</sub> pressures of 5000 to 11,000 Pa, using a conventional volumetric method. Experimental data were treated according to classic kinetic models, Elovich's model being the most adequate for these data. There are two different and successive adsorption processes which can be attributed to sites either energetically or structurally different. Estimated activation energies were 3.9 and 9.3 kcal/mol. Furthermore, for times longer than 70 min, at temperatures higher than 573 K a diffusion mechanism of reticular vacancies appears to control the global kinetics. Diffusion coefficients and activation energy were calculated for the process. The activation energy was 15 kcal/mol. © 1987 Academic Press, Inc.

### INTRODUCTION

The adsorption phenomenon on catalyst surfaces has been widely studied. During the last few years significant advances were achieved due to the development of several new techniques for the analysis of surfaces and adsorbed species.

The O<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> system has been widely investigated. Nevertheless, there are few studies on the chemisorption kinetics of O<sub>2</sub> on this catalyst. Calderbank (1) investigated oxygen equilibrium conditions on a commercial V<sub>2</sub>O<sub>5</sub> catalyst, by measuring chemisorption rates. He concluded that the adsorption isotherms were fitted by the Langmuir's model, indicating the presence of at least two different types of active sites. From his kinetic studies the process appears to be reversible, the bond chemisorbed oxygen-active site being very weak.

Studies of Simard *et al.* (2) on the oxidation of *o*-xylene on vanadium oxides did not detect adsorption or desorption of O<sub>2</sub> on V<sub>2</sub>O<sub>5</sub> by heating up to 673 K or by cooling to room temperature. Nevertheless, they observed an irreversible oxygen adsorption

on V<sub>2</sub>O<sub>4.34</sub> up to approximately 453 K; this additional quantity was desorbed when room temperature was reached.

The oxygen adsorption rate on different V<sub>2</sub>O<sub>5</sub> catalysts was also studied by Dzisyak *et al.* (3). Their data, obtained at a pressure of 933 Pa within a temperature range of 473 to 773 K, were fitted by Elovich's equation.

Bhattacharyya and Mahanti (4) performed kinetic studies of this system in the temperature range from 393 to 673 K on two different catalysts obtained by vanadyl oxalate and ammonium metavanadate decomposition. One of these catalysts had a greater concentration of V<sup>4+</sup> ions. In both cases the adsorption kinetics followed Elovich's equation.

Stanislaus *et al.* (5) worked with an industrial catalyst at temperatures of 573-626 K and found that data were best represented by Elovich's equation, although the initial adsorption for low coverage could also be described by Langmuir's equation. For high coverage they found evidence that chemisorption is controlled by a diffusional process and therefore they used an equation of transient diffusion to analyze their data.

The state of V<sub>2</sub>O<sub>5</sub> in supported V<sub>2</sub>O<sub>5</sub> is different from that in unsupported V<sub>2</sub>O<sub>5</sub>.

<sup>1</sup> To whom correspondence should be addressed.

Yoshida *et al.* (6) conclude that vanadium oxide on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is present as square-pyramidal VO<sub>5</sub> units, while on SiO<sub>2</sub>, it is found as tetrahedral VO<sub>4</sub> units. Wachs *et al.* (7, 8) concluded that V<sub>2</sub>O<sub>5</sub> supported on TiO<sub>2</sub> (anatase) forms a monolayer of surface vanadia species coordinated to the TiO<sub>2</sub> support as well as small crystallites of V<sub>2</sub>O<sub>5</sub>. These different vanadium coordination species have different catalytic properties.

The purpose of the present study is to investigate the kinetic mechanism of O<sub>2</sub> chemisorption on V<sub>2</sub>O<sub>5</sub> catalyst.

## EXPERIMENTAL

### Materials

V<sub>2</sub>O<sub>5</sub> was obtained by precipitation from a hydrochloric solution of ammonium vanadate ((NH<sub>4</sub>)VO<sub>3</sub>) neutralizing with NH<sub>4</sub>OH as it was previously described (9).

In order to minimize diffusional effects, samples were ground and distributed along the reactor. The weight sample was  $\approx$ 250 mg. Particle diameters, measured by scanning electron microscopy, ranged between 10 and 40  $\mu$ m.

The specific surface of samples was 2.6 m<sup>2</sup>/g; this was the average value of three measurements made according to the BET method with Accusorb Micromeritics equipment.

### Kinetic Measurements

Kinetic measurements were performed in a conventional volumetric apparatus of Pyrex glass. A reactor of silica glass was used to avoid formation of vanadium bronze (10).

Oxygen pressures were measured with an MKS capacitance manometer 310 BHS. Since the pressure values obtained were affected by thermal transpiration, they were corrected using an apparent volume method at different working temperatures measured with N<sub>2</sub> (11).

As it was pointed out in a previous report (12), the superficial stabilization of transi-

tion metal oxides is very important in adsorption experiments. Since V<sub>2</sub>O<sub>5</sub> has a tendency to lose oxygen easily, samples must be standardized before each determination. To this end samples were subjected to consecutive runs under either oxidating (1 atm of O<sub>2</sub> at 773 K for 1 h) or reducing (vacuum of  $1.3 \times 10^{-4}$  Pa and 773 K for 45 min) conditions in order to attain the reversibility range. This process has been described previously (12).

After pretreatment, the reactor temperature was brought to the working temperature (473–723 K) and the system was allowed to reach the equilibrium pressure (13). After an initial oxygen pulse was admitted to the reactor (this pulse varied between 5000 and 11,000 Pa according to the measurement temperature), the adsorption rate was measured continuously by recording pressure changes of the system while the gas was adsorbed by the catalyst. The initial pressure was selected according to the system adsorption isotherms previously obtained in this laboratory (12). In this way, when the kinetic measurement was finished the pressure of the system was still higher than that necessary to reach maximum coverage at each temperature.

Each run was repeated at least three times; data were reproducible within 10%.

## RESULTS AND DISCUSSION

Kinetic measurements of oxygen chemisorption on V<sub>2</sub>O<sub>5</sub> were made at 473, 523, 573, 623, 673, and 723 K. Figure 1 shows the values obtained.

Treatment of data was performed with each of the following equations: Langmuir (14), Elovich (14), Troesch (14), and Bangham (14). The best fit was obtained with Elovich's equation

$$\frac{dq}{dt} = a \exp(-bq), \quad [1]$$

where  $q$  is the adsorbed quantity at time  $t$  and  $a$  and  $b$  are constants representing the

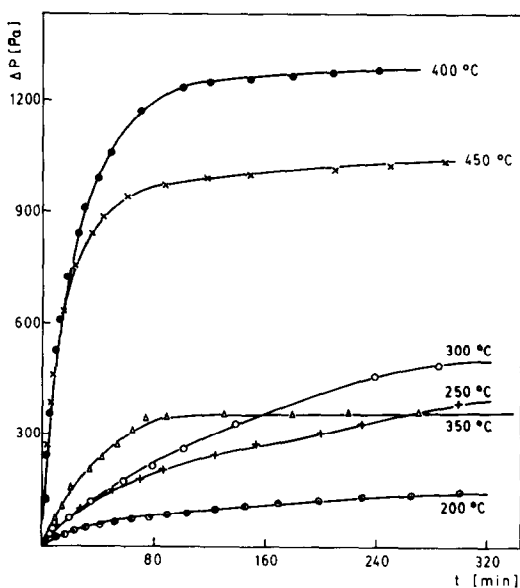


FIG. 1. Experimental results of chemisorption kinetics of O<sub>2</sub> on V<sub>2</sub>O<sub>5</sub>.

initial rate and deceleration coefficient of the process, respectively.

Low (15), Taylor and Thon (16), Aharoni and Tompkins (17), and other authors have demonstrated that Eq. [1] is applicable to adsorption processes on a great number of catalysts.

Such applicability is generally tested by using the integrated form

$$q = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t + t_0), \quad [2]$$

where  $t_0$  is an arbitrary constant originating from integration and which is empirically determined as the value which makes linear the plot of  $q$  vs  $\ln(t + t_0)$ .

Figure 2 shows experimental data represented according to Eq. [2]. Two different behaviors are exhibited within the temperature range 473–623 K, while only one behavior is observed at temperatures of 623, 673, and 723 K. However, at these three latter temperatures, the experimental values deviate from the mentioned behavior when the measurements are made at times longer than 70 min.

These discontinuities have been noted by

several authors (15, 18–21) who explained them on the basis of adsorbate and adsorbent nature, superficial heterogeneities, and pressure and temperature conditions.

Taking into account the critical remarks made by Aharoni (22) on the reports describing this type of behavior, the “S-shaped  $z-t$  plot” model has been used here to represent our experimental values, but the fit was not satisfactory. Kinetic isotherms obtained in this work do not correspond to any of the types included in his classification.

Values of constants  $a$  and  $b$  in Elovich’s equation are given in Table 1 together with the corresponding  $t_0$  values.

Several authors (17, 23) have observed initial instantaneous adsorption previous to adsorption processes which can be represented by Eq. [2]. Cimino *et al.* (23) have modified this equation, obtaining the expression

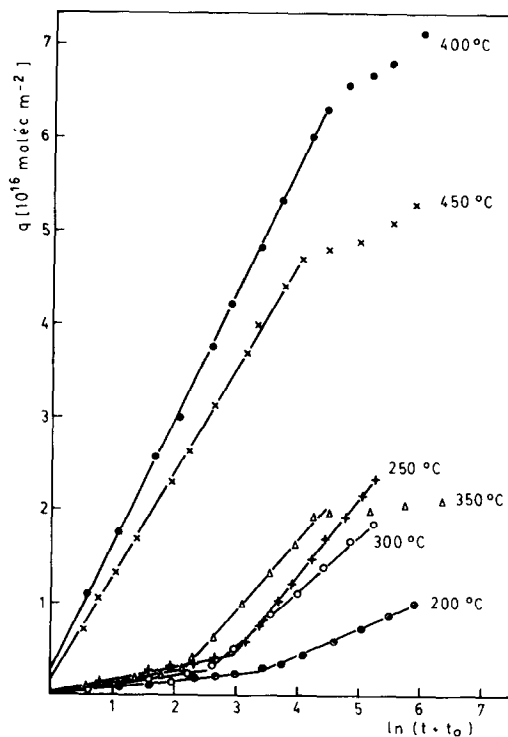


FIG. 2. Elovich’s plot for chemisorption of O<sub>2</sub> on V<sub>2</sub>O<sub>5</sub>.

TABLE I  
 Elovich's Constants

<i>T</i> (K)	<i>a</i> (mol min <sup>-1</sup> )	<i>b</i> (mol <sup>-1</sup> )	<i>a</i> <sub>I</sub> (mol min <sup>-1</sup> )	<i>b</i> <sub>I</sub> (mol <sup>-1</sup> )	<i>a</i> <sub>II</sub> (mol min <sup>-1</sup> )	<i>b</i> <sub>II</sub> (mol <sup>-1</sup> )	<i>t</i> <sub>0</sub> (min)
723	0.117	3.9					1.14
673	0.065	5.1					1.08
623			0.026	18.4	0.027	6.0	1.04
573			0.018	36.9	0.015	8.6	1.10
523			0.012	46.4	0.007	12.3	1.06
473			0.010	27.9	0.004	14.8	1.08

$$q = q_0 + \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t + t_0). \quad [3]$$

Using Eq. [3] and the constants of Table I,  $q_0$  values were estimated at each temperature.

Considering a coverage degree  $\theta$  defined as  $\theta = q/q_s$ , where  $q_s$  is the maximum adsorbed quantity at each temperature, previously reported (12), values of  $\theta = q_0/q_s$  and  $\theta_i$  values corresponding to segment intersections I and II were calculated; they are shown in Table 2. The behavior change I-II occurs at a constant value of  $\theta$  ( $\theta_i \approx 0.06$ ). The  $\theta_0$  corresponding to temperatures below 623 K are considered zero since their values are within the experimental error ( $\pm 0.01$ ). Besides,  $\theta_0$  values corresponding to 673 and 723 K coincide with the value of  $\theta_i$  (I-II).

Figure 3 shows the plot of  $\ln a$  vs  $1/T$ ; from its slope the activation energy can be estimated. The points corresponding to temperatures 673 and 723 K are in line with

those corresponding to the process II thus implying equal value of activation energy. This, together with the fact that  $\theta_0$  at 673 and 723 K coincides with the  $\theta_i$  (I-II), allows one to conclude that at these temperatures the process I is very fast and consequently, the registered values correspond to process II.

The existence of two different behaviors, I and II, and the constancy that  $\theta$  values as a limit between them would take place, occur because of (a) the presence of two energetically different sites ( $V^{3+}$  and  $V^{4+}$ ) (24), or (b) two structurally different sites ( $V_{\Delta}$ , V-O-V) (25). The presence of at least two different active sites has been already proposed by Calderbank (1).

The activation energy of adsorption cal-

TABLE 2		
Calculated Coverage Degree		
<i>T</i> (K)	$\theta_0$	$\theta_i$ (I-II)
723	0.06	
673	0.06	
623	0.006	0.05
573	0.009	0.06
523	0.006	0.05
473	0.007	0.06

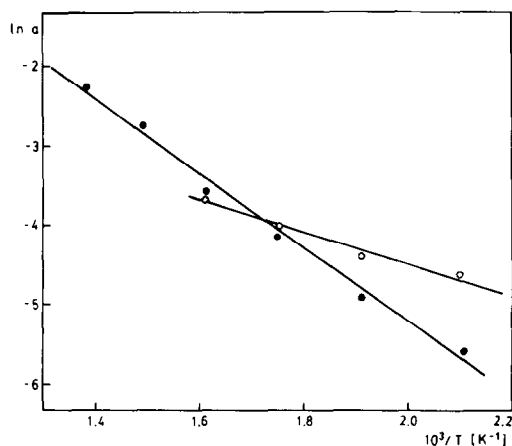


FIG. 3. Initial rate (Elovich) as a function of temperature.

culated by Dzisyak *et al.* (3) was 10 to 15 kcal/mol, depending on the sample used.

Battacharyya and Mahanti (4) explained their results as being indicative of the presence of only one type of chemisorption interaction; they obtained  $E$  values for the adsorption process ranging between 6.4 and 15.5 kcal/mol, but depending both on the catalyst and on the pressure to which the system was subjected.

The activation energy calculated by Stanislaus *et al.* (5) was 6 kcal/mol.

Simard *et al.* (2) obtained an activation energy of 45 kcal/mol which is appreciably greater than that mentioned above. This difference is probably due to the fact that they worked on a more reduced phase (V<sub>2</sub>O<sub>4.34</sub>).

Activation energies of chemisorption obtained in our experiments were 3.9 and 9.3 kcal/mol for the processes I and II, respectively. These values are similar to those found in the mentioned studies.

According to Fig. 2 there is a change of behavior at times of ca. 70 min for 623 K and higher temperatures.

A diffusion mechanism of oxygen vacancies from the bulk to the surface is proposed as the process which controls the rate in this stage. The rate equation proposed to describe this behavior is a relationship of transient diffusion (5),

$$\frac{dN}{dt} = \frac{\Delta c}{\sqrt{\pi d}} \sqrt{\frac{D}{t}}, \quad [4]$$

where  $\Delta c$  is the driving force for diffusion given by the difference of defect concentration between the surface and the interior, and  $d$  is the diffusion distance.

To determine the  $\Delta c$  value when the system is in the state of initial equilibrium ( $P_e$ ), it is first assumed that the concentration of vacancies in superficial layers ( $c_s$ ) is equal to the concentration in the interior of the solid particles ( $c_i$ ). This is due to the fact that at the mentioned temperatures (Tammann temperature = 482 K) we can consider that the crystal atoms are sufficiently mo-

bile so as to allow atom and electron rearrangements starting from a vacancy equilibrium between the solid mass and the superficial layers.

After the pressure pulse  $P_i$ , the surface vacancies are being covered due to the O<sub>2</sub> adsorption and  $c_s$  decreases tending to zero.  $c_i$  remains unchanged and consequently the driving force increases while the chemisorption process advances. When the rate begins to be controlled by the diffusion (change of kinetic behavior) it can be considered that all surface vacancies have been covered; then  $c_s \approx 0$  and  $\Delta c = c_s - c_i = c_i$ .

The  $c_s$  value can be estimated by assuming a direct relationship between the quantity of adsorbed oxygen and the number of vacancies or sites available for adsorption,  $c_s = c_i = 2N_{\text{ads}}$ , where  $N_{\text{ads}}$  is the number of molecules adsorbed up to the time in which the period limited by diffusion begins. The factor 2 appears because a molecule is adsorbed on two sites (12). If we define  $P_{\text{id}}$  as the pressure corresponding to the beginning of such a period taking into account the method of measurement used ( $V = \text{const}$ ) and assuming an ideal behavior, we can conclude that the impelling force for the diffusion is given by

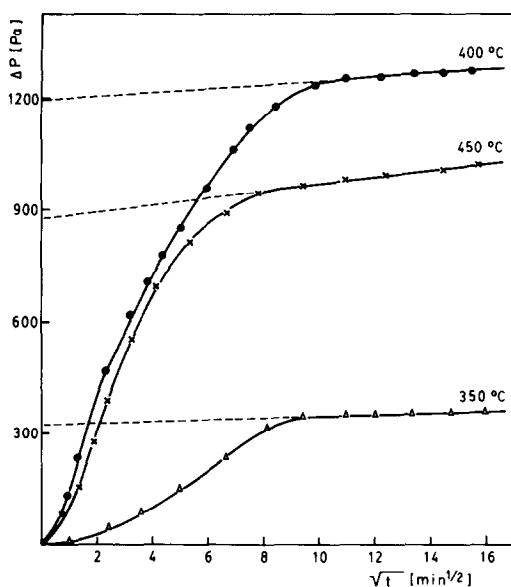
$$\Delta c = \frac{-2(P_i - P_{\text{id}})VN_{\text{ads}}}{RT} \quad [5]$$

Replacing this in Eq. [4] the following is obtained:

$$\frac{dP}{dt} = \frac{-2(P_i - P_{\text{id}})}{\sqrt{\pi d}} \sqrt{\frac{D}{t}}. \quad [6]$$

The diffusion distance “ $d$ ” can be taken as a first approximation equal to the average radius of the catalyst particles. This is because the difference in vacancy concentration between the superficial layers and the interior of the particle was taken into consideration in order to estimate  $\Delta c$ .

Integrating Eq. [6] with the starting point of the diffusional period as the lower limit ( $P_{\text{id}}$ ,  $t_{\text{id}}$ ) we obtain

FIG. 4.  $\Delta P$  vs  $t^{1/2}$ .

$$P_{id} - P = 2k_1(t^{1/2} - t_{id}^{1/2}), \quad [7]$$

where

$$k_1 = \frac{2(P_i - P_{id})}{\sqrt{\pi d}} \sqrt{D}. \quad [8]$$

The  $P_{id}$  value is obtained by extrapolation at  $t = 0$  of the linear zone of graph  $P$  vs  $t^{1/2}$  (Fig. 4) in order to avoid uncertain-

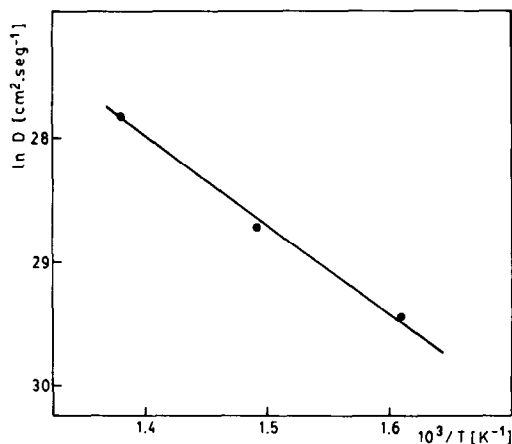


FIG. 5. Diffusion coefficient as a function of temperature.

ties due to the possible existence of a period of nonnegligible mixed control.

This analysis allows one to estimate a mean diffusion coefficient  $D$ .

Thus, mean diffusion coefficients were obtained and are plotted in Fig. 5 as  $\ln D$  vs  $1/T$ . The activation energy for the diffusion of vacancies in the solid phase was 15 kcal/mol.

It is important to note that if the vacancy concentration difference between the surface and the interior is not negligible as pointed out by Haber (26),  $D$  values vary while the value obtained from  $Ed$  remains unchanged.

#### CONCLUSIONS

Oxygen chemisorption on  $V_2O_5$  was measured. Results obtained confirm the adsorption model proposed previously (12).

Experimental data were examined according to classic kinetic models. Elovich's model showed the best fit with the data.

This model indicates that there are two consecutive and different adsorption processes which are the result of sites either energetically or structurally different. Activation energies were 3.9 and 9.3 kcal/mol, respectively.

Furthermore, for times longer than 70 min with temperatures higher than 573 K, a diffusion mechanism of reticular vacancies appears to control the global kinetics.

The mean diffusion coefficient and the activation energy of 15 kcal/mol were calculated for the process.

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