JOURNAL OF CATALYSIS 66, 316–325 (1980)

ESR Investigation of the Redox Processes Occurring upon Oxygen and Propylene Interaction with V_2O_5

ADAM BIELAŃSKI, KRYSTYNA DYREK, AND EWA SERWICKA

Institute of Chemistry, Jagiellonian University, Krupnicza 41, 30-060 Krakow, Poland

Received August 14, 1978; revised April 24, 1980

ESR and chemical analysis were used to investigate the changes in reduction degree of vanadium pentoxide upon interaction with oxygen and propylene. It may be derived from our measurements that the redox processes accompanying interaction of oxygen at temperatures not exceeding 200°C and propylene at temperatures up to 100°C with partially reduced V_2O_5 are restricted to the surface layers only. Assuming a model of two consecutive reactions of the first order the rate constants of the two-step oxidation processes, $V^{3+} \xrightarrow{O_2} V^{4+} \xrightarrow{O_2} V^{5+}$, and two-step reduction processes, $V^{5+} \xrightarrow{C_3H_6} V^{4+} \xrightarrow{C_3H_6} V^{3+}$, were calculated by means of computer optimization. The kinetic data indicate that the activation energies of these reactions are 6.3 and 21 kJ/mol for the first and second steps of oxidation whereas for the first and second steps of reduction they are 33 and 59 kJ/mol, respectively. At temperatures exceeding 200°C the rate of vanadium oxidation is determined by diffusion, the apparent activation energy of this process being 126 kJ/mol.

INTRODUCTION

It has been observed (*1–3*) that vanadium pentoxide is catalytically inactive in the oxidation of hydrocarbons unless the preparation contains a certain amount of vanadium of oxidation state lower than +5. The presence of vanadium(IV) in the partially reduced V_2O_5 makes its appearance in the ESR spectrum registered at room temperature. The partial reduction of vanadium to oxidation state +3 by heat treatment *in vacuo* was postulated by Gillis and Boesman (*4*) in the case of V_2O_5 monocrystals and by Dyrek (*5*) in the case of polycrystalline vanadium oxide preparations. The concentration of vanadium ions in a particular oxidation state evidently influences the adsorption of reagents on V_2O_5 and in consequence determines the reactivity of the system. Thus, for example, Bhattacharyya and Mahanti (*6*) stated that the kinetics of oxygen adsorption on V_2O_5 depended on the vanadium reduction degree. On the other hand Valdelièvre *et al.* (*7*) have shown by means of the ESCA technique that adsorption of propylene on V_2O_5 is accompanied by a change in the vanadium oxidation state. A knowledge of the redox processes occurring in the catalyst upon adsorption of the reactants is essential for the proper understanding of the mechanism of catalytic oxidation of hydrocarbons. For this purpose studies of oxygen and propylene adsorption on vanadium pentoxide catalyst were undertaken in the present research. ESR and chemical analysis were used to follow the changes in the oxidation degree of vanadium in the course of the experiments which enabled simultaneous determination of V^{5+}, V^{4+} and V^{3+} ions.

EXPERIMENTAL

Materials. The preparations of partially reduced V_2O_5 were obtained by thermal decomposition of NH_4VO_3 (pure; Reachim, USSR) *in vacuo* at 350°C. After outgassing at room temperature for 1 h (final pressure 10^{-3}–10^{-4} Pa) the samples were heated to 350°C (6.5 h) and maintained at this temperature under 10^{-3}–10^{-4} Pa for 4 h. Subsequently the ampoules containing the samples were sealed off from the vacuum line and connected by another seal with a glass breaker to the apparatus in which the adsorption and ESR investigations were car-

0021-9517/80/120316-10$02.00/0

ried out. The BET specific surface area of the preparations was 20 m^2/g. In all experiments 15.0-mg samples (surface area 0.3 m^2) were used.

Procedure. Pure gases (POCh Factory, Poland) were used for adsorption experiments. Oxygen adsorption was carried out at temperatures of 100–370°C under a pressure of 10 kPa on partially reduced samples. Propylene adsorption was studied at 100–300°C under the same pressure on the samples partially reduced and also on the samples which were oxidized for 20 h at 300°C in oxygen, thus reaching stoichiometric composition.

After a certain period of contact with gaseous adsorbates the samples were quickly cooled in the closed ampoules to room temperature, transferred into the ESR spectrometer, and the signal measured. Then the ampoule (always closed) was again heated for a certain period of time, cooled, and the ESR signal measured again, etc. In some cases the samples were taken for chemical analysis after ESR measurements.

Chemical analysis. The degree of reduction of the investigated preparations was determined manganometrically after dissolving the samples in a small amount of H_2SO_4 (1 : 1) in a stream of purified nitrogen. The total content of vanadium was subsequently determined by the reduction of V^{5+} to V^{4+} ions using gaseous SO_2 followed by titration with $KMnO_4$. Chemical analysis does not distinguish between vanadium in different oxidation states, and therefore the calculations were made assuming formally that besides V^{5+} only V^{4+} ions were present in the samples. The relative standard deviation $(s_1/y_1) \times 100$ of the analytical determination of the number of V^{4+} averaged over the y_1 values measured was estimated as 0.4%.

ESR spectra. The ESR spectra of the samples were recorded at room and liquid-nitrogen temperatures by using an X-band spectrometer constructed at the Telecommunication and Acoustics Department, Technical University of Wrocław. Polycrystalline $VOSO_4$ was applied as a standard of spin density. The first-derivative spectra of partially reduced V_2O_5 and $VOSO_4$ were recorded one after the other at the same conditions. Interchange of the samples did not affect the Q factor of the cavity. The ESR signals of both partially reduced V_2O_5 and $VOSO_4$ showed similar lineshapes, comparable linewidths, and the same relaxation characteristics. The spectra were recorded in a sweep range 10 times greater than the linewidth. The output signal was sampled at time intervals of 2 sec (0.01 of the sweep time) and its BCD coded values were punched on a paper tape. Double integration of the first-derivative spectrum was performed by means of an Algol program with automatic correction for baseline drift (*8*).

The number of spins in the samples of partially reduced V_2O_5 was calculated on the basis of the following data:

—concentration of V^{4+} ions in $VOSO_4$ standard as determined analytically, and

—ratio of areas under doubly integrated ESR signals of the V_2O_5 sample and $VOSO_4$ standard.

The relative standard deviation $(s_2/y_2) \times 100$ of the determination of the number of spins in partially reduced V_2O_5 performed according to the given procedure averaged over the y_2 values measured amounted to 1.3%. It was calculated from the expression:

$$\frac{s_2}{y_2} = \left(\left(\frac{s_R}{R}\right)^2 + \left(\frac{s_{m_1}}{m_1}\right)^2 + \frac{1}{k_1}\left\{\left(\frac{s_{v_1}}{v_1}\right)^2 + \left(\frac{s_{m_2}}{m_2}\right)^2 + \frac{1}{k_2}\left[\left(\frac{s_{v_2}}{v_2}\right)^2 + \left(\frac{s_{m_3}}{m_3}\right)^2\right]\right\}\right)^{1/2}.$$

In the above formula s_R/R denotes the relative standard deviation of the determination of the ratio of areas (R) under doubly integrated signals of the V_2O_5 and $VOSO_4$ samples; s_{m_1}/m_1, s_{m_2}/m_2, s_{m_3}/m_3 are the relative standard deviations of the weighing, with $VOSO_4$ used as standard for ESR, $VOSO_4$ used for analytical determination of V^{4+}, and $Na_2C_2O_4$ used as standard for manganometric titration, respectively; s_{v_1}/v_1, s_{v_2}/v_2 are the relative standard deviations of the determination of volume of $KMnO_4$ solution used for titration of $VOSO_4$ and $Na_2C_2O_4$ samples, respectively; and k_1, k_2 are the number of replicates.

In the calculations based on both ESR and analytical data the relative standard deviation $(s_3/y_3) \times 100$ averaged over the y_3 values measured was estimated as 1.5% by use of the formula:

$$\frac{s_3}{y_3} = \left(\left(\frac{s_1}{y_1}\right)^2 + \left(\frac{s_2}{y_2}\right)^2\right)^{1/2}.$$

In the calculation of the confidence intervals a normal distribution of the measurement results has been assumed.

RESULTS AND DISCUSSION

1. DEGREE OF THE CATALYST REDUCTION

Fresh catalyst prepared by the vacuum decomposition of NH_4VO_3 at 350°C showed at room temperature an ESR signal with $g = 1.960 \pm 0.005$ and a peak-to-peak linewidth ΔB_{pp} of about 16 ± 1 mT, indicating the presence of vanadium in the oxidation state +4 (*9, 10*). The degree of the catalyst reduction calculated from the number of free spins determined by the double integration of ESR spectra amounted to 1.47 ± 0.05% V^{5+} ions reduced to V^{4+}, whereas that calculated from the chemical analysis data, assuming that besides V^{5+} only V^{4+} ions are present in reduced V_2O_5, was equal to 7.20 ± 0.06%. The deficit in the number of spins determined by the ESR method as compared with the value expected on the basis of analytical data may arise for several reasons: partial reduction of vanadium to the "non-Kramers" V^{3+} ions, different coordination and hence different relaxation characteristics of V^{4+}, and/or presence of mobile electrons in the conduction band of partially reduced V_2O_5. The investigation of ESR spectra at liquid-nitrogen and room temperatures has shown that in this temperature range the ratio of the integrated signal intensity of partially reduced V_2O_5 with respect to that of the $VOSO_4$ standard remains constant, which excludes the two latter possibilities. It may therefore be concluded that the observed deficit in the number of spins results from the partial reduction of vanadium to V^{3+} ions not detectable by ESR and therefore the chemical analysis data represent, as a matter of fact, the sum of $(N_{V^{4+}} + 2\ N_{V^{3+}})$, where $N_{V^{4+}}$ and $N_{V^{3+}}$ denote the numbers of V^{4+} and V^{3+} ions in the sample, respectively. The average composition of the investigated vanadium oxide catalyst is thus given by the formula:

$$V^{5+}_{0.957}V^{4+}_{0.015}V^{3+}_{0.028}O_{2.465}.$$

An alternative model of the observed facts might be to assume that some V^{4+} ions form magnetically coupled pairs. In such a case the formula of the nonstoichiometric oxide would be $V^{5+}_{0.930}V^{4+}_{0.015}(V^{4+}\text{–}V^{4+})_{0.0275}O_{2.465}$. The discrimination between the two models is, however, not possible on the basis of the present results.

2. INTERACTION OF OXYGEN WITH PARTIALLY REDUCED V_2O_5

Figure 1 represents the influence of oxygen adsorption on the V^{4+} ion concentration in partially reduced V_2O_5 as determined from the ESR spectra. The curves describing adsorption in the temperature range not exceeding 200°C are similar. The intensity of the signal attributed to V^{4+} ions initially increases, passes through a maximum, and finally becomes constant. In the course of oxygen adsorption no new signals which might be attributed to the paramagnetic oxygen species appear in the ESR spectrum.

The observed changes in the V^{4+} ion signal intensity may be explained assuming that its initial increase corresponds to the oxidation of the "non-Kramers" V^{3+} ions to V^{4+} ions detectable by ESR, whereas the subsequent decrease is connected with the

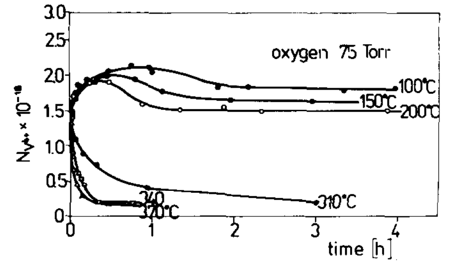

FIG. 1. Dependence of the number of V^{4+} ions ($N_{V^{4+}}$) determined from ESR spectra of partially reduced V_2O_5 on the time of interaction with oxygen at temperatures of 100–370°C. (Total number of V atoms in the sample, 1.03×10^{20}. ESR spectra registered at room temperature.)

oxidation of the V^{4+} ions to diamagnetic V^{5+} ions:

$$V^{3+} \underset{k_a}{\overset{O_2}{\rightarrow}} V^{4+} \underset{k_b}{\overset{O_2}{\rightarrow}} V^{5+}. \qquad (1)$$

The increase in the V^{4+} ion ESR signal is also compatible with the magnetically coupled V^{4+} pairs model. However, it is necessary to assume additionally that each V^{4+}–V^{4+} pair is oxidized in two consecutive steps:

$$(V^{4+}\text{–}V^{4+}) \overset{O_2}{\rightarrow} V^{5+} + V^{4+} \overset{O_2}{\rightarrow} 2V^{5+}.$$

The data concerning adsorption at 100°C are given as an example in Table 1. It is seen that the final decrease in the concentration of V^{3+} ions amounted to 0.91 ($\pm$0.06) $\times$ 10^{18}/15.0-mg sample. This indicates that V^{3+} ions accessible for the oxidation at 100°C represent roughly 20% of the vanadium atoms at a degree of oxidation lower than 5. Also at 200°C the accessibility of V^{3+} ions does not increase appreciably, thus showing that the oxidation was restricted to the near-surface layers.

At temperatures exceeding 300°C the oxidation of vanadium occurs much faster than in the temperature range 100–200°C. The V^{4+} ion ESR signal intensity decreases monotonically down to the value corresponding to a very low degree of reduction. It seems reasonable to assume that at these conditions the oxidation takes place not only in the surface layers but also in the bulk of the crystallites and that diffusion in

TABLE 1

Chemical Analysis and ESR Data Concerning Interaction of Oxygen with Partially Reduced V_2O_5 at 100°C[a]

Adsorption time (min)	$y = (N_{V^{4+}} + 2N_{V^{3+}}) \pm 2s_1$ (from chemical analysis) $2s_1 = 0.06 \times 10^{18}$	$y = N_{V^{4+}} \pm 2s_2$ (from ESR) $2s_2 = 0.05 \times 10^{18}$	$y = N_{V^{3+}} \pm 2s_3$ (from chemical analysis and ESR) $2s_3 = 0.06 \times 10^{18}$	Number of V^{3+} ions oxidized upon oxygen adsorption
1	2	3	4	5
0	7.34×10^{18}	1.55×10^{18}	2.89×10^{18}	—
4	—	1.68×10^{18}	—	—
8	—	1.88×10^{18}	—	—
18	—	1.93×10^{18}	—	—
28	—	2.07×10^{18}	—	—
45	6.32×10^{18}	2.16×10^{18}	2.08×10^{18}	$0.81(\pm 0.06) \times 10^{18}$
58	—	2.12×10^{18}	—	—
60	6.14×10^{18}	2.06×10^{18}	2.04×10^{18}	$0.85(\pm 0.06) \times 10^{18}$
118	—	1.85×10^{18}	—	—
130	5.83×10^{18}	1.85×10^{18}	1.99×10^{18}	$0.90(\pm 0.06) \times 10^{18}$
200	5.77×10^{18}	1.80×10^{18}	1.98×10^{18}	$0.91(\pm 0.06) \times 10^{18}$
238	—	1.84×10^{18}	—	—

[a] Total number of V atoms in the sample, $1.030 \pm 0.007 \times 10^{20}$. $N_{V^{4+}}$ and $N_{V^{3+}}$, number of V^{4+} and V^{3+} ions in the sample, respectively. The confidence interval of the measured value $y \pm 2s$ (s, standard deviation averaged over the y values measured) corresponds to 0.95 probability level.

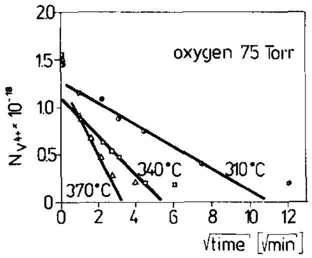

FIG. 2. Dependence of the number of V^{4+} ions ($N_{V^{4+}}$) in a sample of partially reduced V_2O_5 on the square root of the interaction time with oxygen at 310, 340, and 370°C.

the solid phase is the rate-determining step of this process. As Fig. 2 shows, the concentration of V^{4+} ions decreases linearly with the square root of time. Such kinetics of diffusion might be the result of the laminar form of V_2O_5 crystallites.

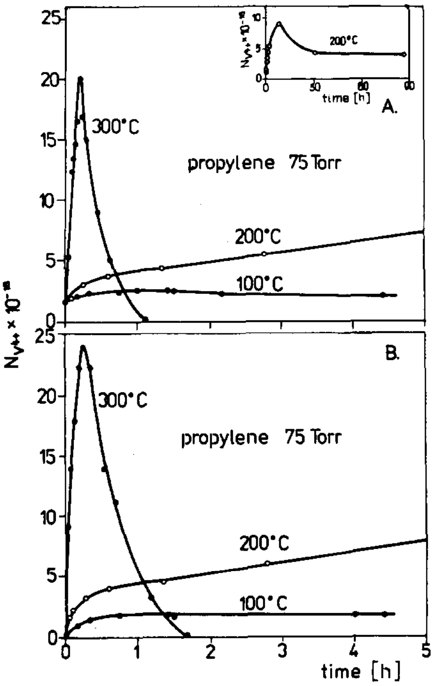

FIG. 3. Dependence of the number of V^{4+} ions ($N_{V^{4+}}$) determined from ESR spectra of partially reduced (A) and oxidized (B) samples on the time of interaction with propylene at 100, 200, and 300°C. Data obtained in the case of a partially reduced sample at 200°C, for a prolonged period of time, are plotted additionally in the inset. (Total number of V atoms in the sample, 1.03 × 10^{20}. ESR spectra registered at room temperature.)

3. INTERACTION OF PROPYLENE WITH V_2O_5

The interaction of propylene with V_2O_5 was studied using both the partially reduced preparation and the stoichiometric one oxidized by heating V_2O_{5-x} in oxygen at 300°C as already described. The changes in the concentration of V^{4+} ions calculated from the ESR signal intensity are shown in Figs. 3A (partially reduced sample) and B (stoichiometric sample) as a function of time. The similar course of the curves indicates that the behavior of the samples during interaction with propylene is analogous in both cases. At 100°C the concentration of V^{4+} ions increases, then passes through a very flat maximum, and after about 1.5 hr reaches a constant level. Chemical analysis confirms the stabilization of the reduction degree after this period of time. At higher temperatures the maxima of the curves representing the changes in the ESR signal intensity are more pronounced. The analytical data show that despite the fact that the V^{4+} content passes through a maximum the reduction degree increases monotonically, which allows us to conclude that the observed shape of the curves is the result of two consecutive processes:

$$V^{5+} \xrightarrow[k_a']{C_3H_6} V^{4+} \xrightarrow[k_b']{C_3H_6} V^{3+}. \qquad (2)$$

The initial increase in the signal intensity is connected with the reduction of V^{5+} to V^{4+} ions whereas its further decrease is due to the subsequent reduction of V^{4+} ions to the "non-Kramers" V^{3+} ions.

If interpreted on the basis of the magnetically coupled pairs model the ESR results would indicate that the concentration of pairs increases strongly with the increase of the total content of V^{4+}.

The smallest changes in the ESR signal intensity were registered at 100°C. The ESR and analytical data concerning the interaction of samples with propylene are summarized in Tables 2 and 3. It is seen that for these conditions reduction was

TABLE 2

Chemical Analysis and ESR Data Concerning Interaction of Propylene with Partially Reduced V_2O_5 at 100°[a]

Adsorption time (min) 1	$y = (N_{V^{4+}} + 2N_{V^{3+}}) \pm 2s_1$ (from chemical analysis) $2s_1 = 0.06 \times 10^{18}$ 2	$y = N_{V^{4+}} \pm 2s_2$ (from ESR) $2s_2 = 0.05 \times 10^{18}$ 3	$y = N_{V^{3+}} \pm 2s_3$ (from chemical analysis and ESR) $2s_3 = 0.06 \times 10^{18}$ 4	Number of V^{5+} ions reduced upon propylene adsorption 5
0	7.34×10^{18}	1.45×10^{18}	2.95×10^{18}	—
10	7.88×10^{18}	1.88×10^{18}	—	—
20	—	2.16×10^{18}	—	—
45	—	2.34×10^{18}	—	—
60	8.81×10^{18}	2.50×10^{18}	3.16×10^{18}	$1.26(\pm 0.06) \times 10^{18}$
85	—	2.49×10^{18}	—	—
90	9.32×10^{18}	2.44×10^{18}	3.44×10^{18}	$1.48(\pm 0.06) \times 10^{18}$
130	9.45×10^{18}	2.34×10^{18}	3.55×10^{18}	$1.49(\pm 0.06) \times 10^{18}$
265	—	2.33×10^{18}	—	

[a] Total number of V atoms in the sample, $1.030 \pm 0.007 \times 10^{20}$. $N_{V^{4+}}$ and $N_{V^{3+}}$, number of V^{4+} and V^{3+} ions in the sample, respectively. The confidence interval of the measured value $y \pm 2s$ (s, standard deviation averaged over the y values measured) corresponds to 0.95 probability level.

very slight and practically stopped after 90 min. Such behavior indicates that the redox processes are restricted to the surface layers of the catalyst. This is supported also by the following calculation concerning the stoichiometric samples of V_2O_5 (Table 3). In this case the total number of V^{5+} ions reduced to V^{4+} ($1.77 \pm 0.05 \times 10^{18}$) and V^{3+} ($0.98 \pm 0.06 \times 10^{18}$) under the influence of propylene at 100°C amounted to $2.75 \pm 0.06 \times 10^{18}$ in a 15.0-mg sample, i.e., $9.2 \pm 0.1 \times 10^{18}/m^2$. This value is comparable with the number of vanadium atoms present on 1 m^2 of the easy-cleavage plane [010] of V_2O_5 calculated from the X-ray data (*11*), namely, $9.8 \times 10^{18}/m^2$.

The changes in V^{4+} content observed at 200 and 300°C were much more pronounced

TABLE 3

Chemical Analysis and ESR Data Concerning Interaction of Propylene with Stoichiometric V_2O_5 at 100°C[a]

Adsorption time (min) 1	$y = (N_{V^{4+}} + 2N_{V^{3+}}) \pm 2s_1$ (from chemical analysis) $2s_1 = 0.06 \times 10^{18}$ 2	$y = N_{V^{4+}} \pm 2s_2$ (from ESR) $2s_2 = 0.05 \times 10^{18}$ 3	$y = N_{V^{3+}} \pm 2s_3$ (from chemical analysis and ESR) $2s_3 = 0.06 \times 10^{18}$ 4	Number of V^{5+} ions reduced upon propylene adsorption 5
0	0	0	0	—
10	—	0.93×10^{18}	—	—
20	—	1.43×10^{18}	—	—
45	3.31×10^{18}	1.80×10^{18}	0.75×10^{18}	$2.55(\pm 0.06) \times 10^{18}$
85	—	1.87×10^{18}	—	—
90	3.81×10^{18}	1.72×10^{18}	1.04×10^{18}	$2.76(\pm 0.06) \times 10^{18}$
240	3.74×10^{18}	1.77×10^{18}	0.98×10^{18}	$2.75(\pm 0.06) \times 10^{18}$
265	—	1.77×10^{18}	—	—

[a] Total number of V atoms in the sample, $1.030 \pm 0.007 \times 10^{20}$. $N_{V^{4+}}$ and $N_{V^{3+}}$, number of V^{4+} and V^{3+} ions in the sample, respectively. The confidence interval of the measured value $y \pm 2s$ (s, standard deviation averaged over the y values measured) corresponds to 0.95 probability level.

and cannot be restricted to the surface layer only, but engage via diffusion processes also the deeper layers of the crystal lattice.

4. KINETICS OF THE REDOX PROCESSES OCCURRING IN THE COURSE OF OXYGEN AND PROPYLENE INTERACTION WITH V_2O_5

4.1. *Oxygen Interaction*

As already stated, the changes in the oxidation state of vanadium occurring at 100–200°C, when oxygen is chemisorbed on partially reduced vanadium pentoxide, are due to the two consecutive reactions represented by Eq. (1). It seems reasonable to assume that both reactions are first order with respect to the concentration of appropriate vanadium ions. All experiments were carried out at quasi-isobaric conditions, which enables us to write the following kinetic equation expressing the rate at which the concentration of V^{4+} ions is changing:

$$\frac{dN_{V_s^{4+}}}{dt} = k_a N_{V_s^{3+}} = K_b N_{V_s^{4+}}. \qquad (2)$$

In this relation $N_{V_s^{3+}}$ and $N_{V_s^{4+}}$ denote the number of particular vanadium ions taking part in the oxidation. The suffix "s" has been added in order to underline that the process engages only surface or near-surface vanadium ions. Thus the changes in the total V^{4+} concentration in the course of chemisorption may be described by the equation:

$$N_{V_{tot}^{4+}}(t) = N_{V_s^{4+}}(0) \times e^{-k_b t} + \frac{k_a N_{V_s^{3+}}(0)}{k_b - k_a}(e^{-k_a t} - e^{-k_b t}) + N_{V_{bulk}^{4+}}. \qquad (4)$$

The values $N_{V_s^{3+}}(0)$ and $N_{V_s^{4+}}(0)$ denote the number of appropriate vanadium ions in the surface layer of the initial sample of partially reduced vanadium oxide. As already stated, the value $N_{V_s^{3+}}(0)$ was 0.91 ± 0.06 × 10^{18} atoms/15.0-mg sample. The value of $N_{V_s^{4+}}(0)$ was calculated to be 0.35 ± 0.06 × 10^{18} from the expression:

$$N_{V_s^{4+}}(0) = N_{V_s} - N_{V_s^{3+}}(0) - N_{V_s^{5+}}(0), \qquad (5)$$

where N_{V_s} (equal to 2.75 ± 0.06 × 10^{18} per sample as stated in Section 3) represents the total number of vanadium atoms in the surface layer and $N_{V_s^{5+}}(0)$ the number of unreduced V^{5+} atoms also in the surface layer. This latter value was determined in an experiment in which an initially partially reduced sample was further reduced by propylene at 100°C (Table 2). The bulk diffusion being very slow at this temperature, the reduction was limited to the surface region and after about 90 min reached a constant level. The increase in the concentration of V^{4+} was then $\Delta N_{V^{4+}}$ = 0.89 ± 0.05 × 10^{18} and the increase in the concentration of V^{3+} $\Delta N_{V^{3+}}$ = 0.60 ± 0.06 × 10^{18}/15.0-mg sample. Hence $N_{V_s^{5+}}(0) = \Delta N_{V^{4+}} + \Delta N_{V^{3+}}$ = 1.49 ± 0.06 × 10^{18} per sample. The number of V^{4+} ions which remain unaffected in the course of chemisorption ($N_{V_{bulk}^{4+}}$ = 1.15 ± 0.06 × 10^{18}) was obtained by subtracting the $N_{V_s^{4+}}(0)$ from the analytically determined total number of V^{4+} ions in the sample. On the basis of Eq. (4) the values of the rate constants k_a and k_b were found by computer optimization of these parameters with respect to the experimental ESR data. The curve calculated from this equation by using the optimized values of rate constants coincides well with the experimental one for each temperature within the discussed region. The experimentally determined dependence of $N_{V^{4+}}$ on the time of oxygen adsorption at 100°C is plotted as an example in Fig. 4A together with the plot of Eq. (4) in which k_a and k_b values estimated by the computer were inserted. Both plots are in good agreement with the exception of the last stage where according to expectation based on the applied model the concentration of V^{4+} ions should diminish more rapidly. The possible explanation of this discrepancy may be inhomogeneity of the V_2O_5 surface which results in retardation of the adsorption process after depletion of the most active centers.

The calculated rate constants k_a and k_b for the temperatures 100, 150, and 200°C are given in Table 4. The activation energies E_a and E_b of the two stages of oxidation, $V^{3+} \xrightarrow{k_a} V^{4+}$ and $V^{4+} \xrightarrow{k_b} V^{5+}$, are 6.3 and 21 kJ mol^{-1}, respectively. The higher values of k_a than k_b in the investigated range of temperature indicate that V^{3+} ions are more active centers of oxygen adsorption than V^{4+} ions.

Oxygen adsorption on partially reduced V_2O_5 at 310–370°C involves in the process of oxidation vanadium ions which are situated not only at the surface or in the near-surface layers but also in the bulk of V_2O_5 crystallites. Such an interpretation explains both the appreciable diminution of the reduction degree of the sample upon oxygen adsorption in this temperature range and the linear dependence of the V^{4+} ion concentration on the square root of the adsorption time, typical for diffusion processes (Fig. 2). If it is assumed that the rate of V^{4+} ion disappearance is determined mainly by the rate of diffusion, i.e., $-dN_{V^{4+}}/dt = V_{diff}$, a relationship between diffusion rate at a given temperature and V^{4+} ion concentration in the sample may be obtained. Differentiating the experimentally established dependence

$$N_{V^{4+}}(t) = -kt + N_{V^{4+}}(0) \qquad (6)$$

gives

$$v_{diff} = \tfrac{1}{2}k^2(N_{V^{4+}}(0) - N_{V^{4+}}(t))^{-1}. \qquad (7)$$

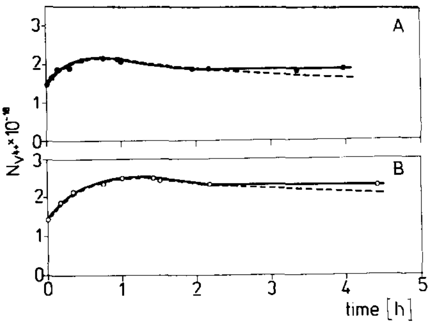

FIG. 4. Experimental (solid lines) and theoretical (dashed lines) curves representing dependence, $N_{V^{4+}} = f$(time), for oxygen (A) and propylene (B) adsorption on partially reduced V_2O_5 at 100°C.

The value of $K = \frac{1}{2}k^2$ may be considered as proportional to the effective coefficient of diffusion into the bulk of V_2O_5. From the values of K for temperatures 310, 340, and 370°C the activation energy of the diffusion process was estimated as E_{diff} = 126 kJ mol^{-1}.

The problem of the nature of diffusing species cannot be solved on the basis of our results. However, it should be remembered that isotopic exchange of bulk oxygen was observed already at 420°C by Kakioka (*12*). In our case a high concentration of defects may facilitate oxygen diffusion also at lower temperatures.

4.2. *Propylene Interaction*

The redox processes occurring in V_2O_5 in the course of interaction with propylene were studied, similarly as with adsorption of oxygen, in quasi-isobaric conditions and

TABLE 4

Rate Constants of the Redox Processes Occurring in the Course of Oxygen and Propylene Interaction with V_2O_5

Oxygen adsorption					Propylene adsorption		
Temp. (°C)	k_a (min^{-1})	k_b (min^{-1})	Temp. (°C)	k (mol min^{-1})	Temp. (°C)	k_a' (min^{-1})	k_b' (min^{-1})
100	0.0514	0.0055	310	1.15×10^{-3}	100	0.0331	0.0037
150	0.0563	0.0119	340	2.04×10^{-3}	200	0.1968	0.5276
200	0.0722	0.0233	370	3.88×10^{-3}	300	1.6648	3.5849

may be also interpreted as the result of two consecutive first-order reactions represented by Eq. (2). The restriction of these redox processes to the surface layers of the catalyst is, however, valid in this case only at 100°C. The rate constants k'_a and k'_b for this temperature were found, as in the case of oxygen adsorption, by optimization of the parameters in the equation:

$$N_{V^{4+}_{tot}}(t) = N_{V^{4+}_s}(0) \times e^{-k'_b t} + \frac{k'_a N_{V^{5+}_s}(0)}{k'_b - k'_a} (e^{-k'_a t} - e^{-k'_b t} + N_{V^{4+}_{bulk}}), \quad (8)$$

where $N_{V^{5+}}(0)$ equal to $1.49 \pm 0.06 \times 10^{18}$ atoms/15.0-mg sample (see Section 4) denotes the number of accessible V^{5+} ions in the initial sample of partially reduced V_2O_5 whereas $N_{V^{4+}_s}$ and $N_{V^{4+}_{bulk}}$ have the same meaning as previously. As is seen from Fig. 4B the curves found on the basis of the theoretical equation and the experimental one have a very similar course.

The rate constants k'_a and k'_b for the propylene adsorption at 200 and 300°C could not be determined in the same way as for the adsorption at lower temperatures because discrimination between bulk and surface concentration on V^{4+} would be necessary. The following procedure was applied in order to obtain an approximate estimate of both constants. The values k'_a and k'_b for the propylene adsorption at 200 and 300°C were found graphically from the plots $N_{V^{4+}} = f(\text{time})$ assuming that the very initial parts of the curves depend mostly on surface processes. The values k'_a were estimated from the graphs describing propylene adsorption on stoichiometric V_2O_5 (Fig. 3B) using the following kinetic equation based on the assumption that in the initial stages V^{4+} ions are formed predominantly:

$$\left(\frac{dN_{V^{4+}_s}}{dt}\right)_0 = k'_a N_{V^{5+}_s}(0). \quad (9)$$

In this relation $N_{V^{5+}_s}(0) = 2.75 \pm 0.06 \times 10^{18}$ (see Section 3) denotes the total number of V^{5+} ions on the surface of the oxidized sample.

The values of the rate constants k'_b were calculated from the adsorption data for partially reduced samples. In this case the following equation was used:

$$\left(\frac{dN_{V^{4+}_s}}{dt}\right)_0 = k'_a N_{V^{5+}_s}(0) - k'_b N_{V^{4+}_s}(0), \quad (10)$$

where $N_{V^{5+}_s}(0) = 1.49 \pm 0.06 \times 10^{18}$ and $N_{V^{4+}_s}(0) = 0.35 \pm 0.06 \times 10^{18}$ correspond to the number of V^{5+} and V^{4+} ions on the surface of the reduced sample before propylene adsorption. The results are given in Table 4. The activation energies for surface processes are respectively: $E'_a = 33$ kJ mol^{-1} for $V^{5+} \xrightarrow{C_3H_6} V^{4+}$ and $E'_b = 59$ kJ mol^{-1} for $V^{4+} \xrightarrow{C_3H_6} V^{3+}$. The comparison of the values k'_a and k'_b for 100°C indicates that in the course of propylene interaction with V_2O_5 at low temperatures the reduction occurs much faster on V^{5+} ions than on V^{4+} ions.

CONCLUSIONS

As already stated, the ESR method has hitherto been used only as a means of detecting V^{4+} ions appearing as the result of V_2O_5 partial reduction. In the present investigation this method combined with classical chemical analysis was applied in a deeper study of the redox processes at the surface of the same oxide. We conclude that the redox processes accompanying oxygen adsorption at temperatures not exceeding 200°C and propylene adsorption up to 100°C are restricted only to the surface layers of the catalyst. At such temperatures reduction of V^{5+} with propylene occurs more rapidly than that of V^{4+}. On the other hand, in the course of oxygen adsorption on partially reduced V_2O_5, V^{3+} is more rapidly oxidized than V^{4+}.

The selective oxidation of hydrocarbons on oxide catalysts is most frequently assumed to occur by the mechanism of Mars and van Krevelen. This comprises the oxidation of the organic molecule by the insertion of lattice oxygen as the first step and the subsequent reoxidation of the reduced catalyst. From our experiments it is seen that this second step is greatly exhanced by the presence of V^{3+} ions and it may be supposed that in a working catalyst representing a high dynamic system a certain concentration of V^{3+} is necessary to ensure fast enough sorption of oxygen.

ACKNOWLEDGMENT

The authors are greatly indebted to Professor A. Rokosz, Jagiellonian University, for his help in statistical evaluation of the results.

REFERENCES

1. Simard, G. L., Steger, J. F., Arnott, R. J., and Siegel, L. A., *Ind. Eng. Chem.* **47,** 1424 (1955).
2. Andreikov, E. I., Skorokhod, V. V., and Rusyanova, N. D., *Kinet. Katal.* **14,** 1189 (1973).
3. Bielański, A., and Inglot, A., *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **22,** 773 (1974).
4. Gillis, E., and Boesman, E., *Phys. Status Solidi* **14,** 337 (1966).
5. Dyrek, K., *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **22,** 605 (1974).
6. Bhattacharyya, S. K., and Mahanti, P., *J. Catal.* **20,** 10 (1971).
7. Valdelièvre, M., Dachy, G., and Leroy, J. M., *C.R. Acad. Sci.* **276,** 1179 (1975).
8. Łagan, J. M., *Rocz. Chem. Ann. Soc. Chim. Pol.* **47,** 199 (1973).
9. Tarama, K., Teranishi, S., Yoshida, S., and Tamura, N., *in* "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," p. 202. Wiley, New York, 1965.
10. Mann, R. S., and Khulbe, K. C., *Bull. Chem. Soc. Japan* **45,** 2929 (1972).
11. Fiermans, L., and Vennik, J., *Surface Sci.* **9,** 187 (1968).
12. Kakioka, H., thesis, University of Lyon, 1969.