JOURNAL OF CATALYSIS **81**, 46–60 (1983)

Electron Spin Resonance Investigation of Oxygen Interaction with V_2O_5–MoO_3 Catalysts

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Received March 18, 1982; revised August 9, 1982

The changes in reduction degree of V_2O_5–MoO_3 catalysts occurring in the course of oxygen adsorption were investigated by electron spin resonance and chemical analysis. Two different types of paramagnetic centers, involving reduced vanadium ions stabilized by oxygen vacancies and substitutional Mo^{6+} ions, have been found in partially reduced catalysts. The kinetics of oxidation of such catalysts investigated by electron spin resonance revealed a delay in oxidation of the centers stabilized by Mo^{6+}. The role of segregation processes occurring upon redox treatment of the V_2O_5–MoO_3 catalysts in determination of the stability of particular centers has been discussed.

INTRODUCTION

The improvement of the selectivity of vanadia catalysts upon addition of MoO_3 in the catalytic oxidation of hydrocarbons is usually related to the formation of the solid solution V_2O_5–MoO_3 containing up to 30 mole% of MoO_3. The recent results of Bielański and Najbar (*1–4*) have shown that the segregation processes occurring in oxidizing or reducing atmosphere may alter the composition of the surface layers of the solid solution. Enrichment with molybdenum accompanies reduction and may even result in the formation of separate phases of the lower oxides of molybdenum. On the other hand, enrichment with vanadium occurs upon oxidation. It may be supposed that the segregation processes will strongly influence the redox properties of the V_2O_5–MoO_3 catalysts.

In the present work, ESR spectroscopy and chemical analysis were applied to investigate oxygen interaction with partially reduced vanadia–molybdena catalysts obtained in a similar way as the previously investigated, partially reduced V_2O_5 (*5*).

EXPERIMENTAL

Materials. The catalysts were prepared by thermal decomposition of a mixture of NH_4VO_3 and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (NH_4VO_3—pure, Reachim USSR; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$—anal. pure, POCh, Poland) *in vacuo* at 10^{-3}–10^{-4} Pa. In order to obtain the mixture of vanadium and molybdenum salts, weighed portions of each of them were dissolved in a diluted aqueous solution of ammonia (anal. pure, POCh). After filtering, both solutions were mixed and evaporated on a water bath to dryness. The samples obtained in this way were passed through a 0.3-mm sieve. The ampoules containing 20–25 mg of the sample ($\sim 10^{20}$ V and Mo atoms) were connected to the vacuum apparatus and after outgassing to 10^{-3}–10^{-4} Pa at room temperature, they were heated at a rate of 3°K/min up to 450°K, and then at a rate of 0.7°K/min up to 623°K. At this temperature, the samples were maintained for 5 h under a pressure of 10^{-3}–10^{-4} Pa. The ampoules were then sealed off from the vacuum line. The preparations obtained in this way will be called "partially reduced."

TG and DTA analyses. Thermogravimetric and differential thermal analyses were performed by means of a Mettler thermoanalyzer Model TA-2 in argon atmosphere with α-Al_2O_3 as a standard. The temperature of decomposition of NH_4VO_3, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and of their mixture

0021-9517/83 $3.00

did not exceed 623°K. Therefore, this temperature was chosen for thermal treatment of the precursors of the V–Mo catalysts in the present work, similarly as previously for NH_4VO_3 (*5*).

X-Ray analysis of powder samples was performed by means of an X-ray diffractometer Model DRON-2 (USSR) using Cu*Kα* radiation.

Chemical analysis. Contents of vanadium and molybdenum in the catalysts were determined by atomic absorption using a Perkin–Elmer spectrometer Model 503. Wavelengths of 313.3 and 318 nm were used for determination of Mo and V, respectively. The results of analyses are given in Table 1.

The total reduction degree of the catalysts was determined manganometrically after dissolving samples in a small amount of H_2SO_4 (1 : 1) in a stream of purified nitrogen. Reduced vanadium and molybdenum ions of various degree of oxidation are not distinguishable by chemical analysis, so the amount of consumed $KMnO_4$ was expressed as the amount of singly reduced (V^{4+} or Mo^{5+}) ions, assuming formally that no deeper reduction proceeds (which is not actually true, as will be shown later). The relative standard deviation $(s_1/y) \times 100$ of the analytical determination of the number of V^{4+} and/or Mo^{5+} ions averaged over the y values measured was estimated as 0.4%.

ESR spectra. The ESR spectra were recorded at room temperature and at 77°K using an X-band spectrometer constructed at the Telecommunication and Acoustics Department, Technical University, Wrocław. The g factors were determined using DPPH as a standard. Polycrystalline $VOSO_4$, which showed ESR parameters similar to those of partially reduced V_2O_5–MoO_3 catalysts, was used as a standard of spin concentration. The ESR signals of both vanadia–molybdena catalyst and $VOSO_4$ were recorded one after another at the same conditions. The output signal was sampled at time intervals of 2 s and its BCD coded values were punched on paper tape. Double integration of the first derivative spectrum was performed by means of a FORTRAN program with automatic correction for base line drift (*6*). The number of spins was calculated from the ratio of areas under doubly integrated ESR signals of the vanadia–molybdena catalyst and $VOSO_4$ standard. The relative standard deviation $(s_2/y) \times 100$ of the determination of the number of spins in partially reduced samples, performed according to the procedure given in Ref. (*5*), averaged over the y values measured amounted to 1.3%. In the calculations based on both ESR and analytical data the relative standard deviation $(s_3/y) \times 100$ averaged over the y values measured was estimated as 1.5%. In the calculation of the confidence intervals a normal distribution of the measurements results has been assumed.

TABLE 1

Composition of the Catalysts and their BET Specific Surface Areas

Catalyst No.	Mole% of V_2O_5	Mole% of MoO_3	BET specific surface area (m^2 g^{-1})
1	100	0	59
2	96.6	3.4	57
3	79.0	21.0	51
4	72.0	28.0	43
5	0	100	38

Raman spectra of the partially reduced and reoxidized: V_2O_5, MoO_3, and V_2O_5–MoO_3 catalysts were recorded using a Varian spectrometer Model 82 with an argon laser. The measurements were performed in the wavenumber range up to 1300 cm^{-1}.

The BET specific surface areas of the catalysts were evaluated from nitrogen adsorption isotherms taken at 77°K. The results are presented in Table 1.

Oxygen adsorption. Oxygen from the decomposition of $KMnO_4$ was used for adsorption experiments carried out in the temperature range of 373–673°K under a pressure of 10 kPa. The pressure of oxygen was practically constant in the course of experiments. After introducing oxygen into ampoules with partially reduced samples, they were heated at a given temperature for a certain period of time. Then the samples were cooled in the closed ampoules to room temperature and the ESR signals were recorded. This procedure was repeated until a constant value of ESR signal intensity was reached. The same procedure of heat treatment was followed before chemical analysis. Some of the partially reduced samples were oxidized for 20 h at 623°K. These samples will be called "reoxidized."

RESULTS AND DISCUSSION

1. Characteristics of the Catalysts

Partially reduced V_2O_5 and MoO_3 obtained by thermal decomposition *in vacuo* from appropriate salts are monophase systems. On the other hand, in the vanadia–molybdena catalysts two phases may be distinguished on the basis of X-ray diffraction data, viz., a solid solution of MoO_3 in V_2O_5 with orthorhombic structure and orthorhombic MoO_3, respectively. The amount of the latter phase increases with increasing MoO_3 content (Table 1).

At room temperature partially reduced V_2O_5 exhibits the ESR signal of V^{4+} ions (*5, 7*) with an intensity corresponding to the reduction degree of 1.29% (Table 2). Partially reduced MoO_3 shows an ESR signal of much lower intensity (Table 2) indicating presence of Mo^{5+} and Mo^{3+} ions.

At room temperature partially reduced V_2O_5–MoO_3 catalysts show an ESR signal with $g = 1.960 \pm 0.005$, characteristic of V^{4+} ions in partially reduced V_2O_5. A peak-to-peak width ΔB_{pp} of the signal depends on the concentration of MoO_3 and decreases from 21.0 ± 0.1 mT for partially reduced V_2O_5 to 16.0 ± 0.1 mT for the samples containing 21.0–28.0 mole% of MoO_3. The catalyst of highest concentration of MoO_3 reveals the highest symmetry and intensity of the ESR signal.

TABLE 2

Reduction Degree of the V_2O_5–MoO_3 Catalysts Calculated from Chemical Analysis and ESR[a]

Treatment	V_2O_5		V_2O_5–MoO_3						MoO_3	
			3.4 mole% MoO_3		21.0 mole% MoO_3		28.0 mole% MoO_3			
	Chem. anal.	ESR	Chem. anal.	ESR	Chem. anal.	ESR	Chem. anal.	ESR	Chem. anal.	ESR
Reduction *in vacuo* at 623°K	8.01 (±0.06)	1.29 (±0.05)	11.78 (±0.09)	1.75 (±0.05)	18.31 (±0.10)	2.60 (±0.05)	20.78 (±0.10)	3.45 (±0.05)	8.86 (±0.06)	0.20 (±0.05)
Reoxidation at 623°K	0	0	2.17 (±0.06)	0.54 (±0.05)	4.03 (±0.06)	1.80 (±0.05)	4.96 (±0.06)	2.30 (±0.05)	0.06 (±0.06)	0.05 (±0.05)

[a] Expressed as percentage of V^{4+} and/or Mo^{5+} ions, assuming that the total number of V and Mo atoms equals 100%. 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.

After reoxidation of partially reduced V_2O_5, the ESR signal of V^{4+} ions disappears completely, whereas in the reoxidized V_2O_5–MoO_3 catalysts the single line disappears and a new signal with hyperfine structure can be observed at 77°K. The latter signal consists of two sets of eight lines, one centered on $g_\perp$ and the other on $g_\parallel$ ($g_\perp = 1.99 \pm 0.01$; $g_\parallel = 1.90 \pm 0.01$; $A_\perp = 4.9 \pm 0.1$ mT; $A_\parallel = 14.4 \pm 0.1$ mT). The hyperfine structure arises from the interaction of the unpaired electron with the nuclear spin of ^{51}V ($I = 7/2$). The parameters of the signal are characteristic for V^{4+} ions coupled with Mo^{6+} in V_2O_5–MoO_3 solid solutions (*8*). It may be thus concluded that in the investigated catalysts, besides the V^{4+} ions stabilized by oxygen vacancies (for which, similarly as in partially reduced V_2O_5, no hyperfine structure is observed due to the dipolar broadening), V^{4+} ions situated in the vicinity of substitutional Mo^{6+} ions are present. With increasing concentration of MoO_3, the intensity of the V^{4+}–Mo^{6+} signal increases and the components of the hyperfine structure broaden. The reduction degree of the reduced and reoxidized samples is given in Table 2.

The analytically determined total number of reduced ions in V_2O_5–MoO_3 catalysts, representing their total reduction degree, calculated on the assumption that only V^{5+}, Mo^{6+} and singly reduced V^{4+} or Mo^{5+} ions are present, is much greater than that calculated from the number of paramagnetic centers determined by ESR (Table 2). The observed difference may arise for several reasons: partial reduction of vanadium and/or molybdenum to the "non-Kramers" (V^{3+} and/or Mo^{4+}) ions not detectable by ESR, different coordination and thus different relaxation characteristics of V^{4+}, or formation of magnetically coupled pairs (V^{4+}–V^{4+} and/or Mo^{5+}–Mo^{5+}) with resulting magnetic moment equal to zero.

The investigation of the temperature dependence of the ESR signal of V_2O_5–MoO_3 catalysts excludes the second and third possibilities. The ratio of the integrated signal intensity of partially reduced V_2O_5–MoO_3 catalysts to that of the $VOSO_4$ standard, which contains V^{4+} exclusively in distorted octahedral coordination, remains practically constant at liquid nitrogen and at room temperature, indicating the same relaxation characteristics and thus similar symmetry for the V^{4+} ions. A similar argument may be used in discussion of the possible formation of the magnetically coupled pairs. The formation of such pairs should be facilitated at low temperatures, thus leading to a decrease of the relative signal intensity with lowering of the temperature, which however was not observed. It may be concluded that the V^{4+}–V^{4+} and/or Mo^{5+}–Mo^{5+} pairs do not contribute significantly to the partial vanishing of the ESR signal of V_2O_5–MoO_3 catalysts.

The other possible explanation of the deficit of V^{4+} ions observed in ESR spectra, as compared with the results of chemical analysis, is the assumption of partial reduction of vanadium and/or molybdenum to the "non-Kramers" ions. The assumption of the presence of V^{3+} ions in partially reduced V_2O_5–MoO_3 catalysts agrees well with the shape of the kinetic curves representing changes of the ESR signal intensity occurring upon interaction with oxygen, which will be discussed later.

Some evidence of the presence of "non-Kramers" Mo^{4+} ions in the investigated catalysts may be obtained from Raman spectra. Besides the bands characteristic of vibrations of chemical bonds in V_2O_5 and MoO_3 crystals (*9*), the reduced and reoxidized V_2O_5–MoO_3 catalysts exhibit an additional band with a Raman shift $\Delta\nu$ equal to 1100 cm^{-1}. The intensity of the band at 1100 cm^{-1} somewhat decreases upon oxidation at 623°K. This band is observed also in the Raman spectrum of partially reduced MoO_3 but, unlike that in V_2O_5–MoO_3 catalysts, it disappears completely after oxidation. The total reduction degree of partially reduced MoO_3, determined by chemical analysis (Table 2), is higher than that calculated from ESR spectra, thus indicating that besides Mo^{5+} and Mo^{3+} ions detectable by ESR reduced molybdenum ions not detectable by ESR are present in this sample. Since in reoxidized MoO_3 such a deficit is not observed and only Mo^{5+} and Mo^{3+} ions detectable by ESR are present, it may be concluded that the 1100 cm^{-1} band in the Raman spectrum of partially reduced MoO_3 is connected with the vibrations of the chemical bonds in the centers not detectable by ESR, e.g., Mo^{4+} ions or magnetically coupled Mo^{5+}–Mo^{5+} pairs. Vibrations of metal–metal bonds are represented by bands in the region of low frequencies of Raman spectra (*9*) and so the 1100 cm^{-1} band cannot be attributed to such pairs. The 1100 cm^{-1} band may be thus connected with the vibrations of chemical bonds of Mo^{4+} ions with oxygen. Hence, the presence of Mo^{4+} ions in partially reduced as well as in reoxidized vanadia–molybdena catalysts is assumed.

2. *Oxygen Adsorption*

Figures 1–3 show the dependence of the concentration of paramagnetic centers, calculated from ESR spectra of V_2O_5–MoO_3 catalysts, on the time of oxygen adsorption. The curves describing changes in the intensity of the ESR signal in the temperature range 373–473°K pass through two maxima and after a certain period of time attain a constant level. No new signals which might be attributed to the paramagnetic oxygen species appear in the ESR spectrum. At a given temperature, the position of the first maximum is practically independent of the content of molybdenum whereas the position of the second maximum shifts toward shorter adsorption time upon increasing MoO_3 concentration. The number of spins corresponding to the constant level depends on both the temperature and the concentration of MoO_3. With increasing temperature, the concentration of the paramagnetic centers corresponding to the plateau decreases, whereas at a given temperature it becomes higher upon increasing MoO_3 content.

In the temperature range 573–673°K, the intensity of the ESR signal initially decreases upon interaction with oxygen, then passes through only one maximum and finally becomes constant. The position of the maximum depends on the MoO_3 concentration, similarly to that of the second maximum appearing at lower temperatures. Most probably, the increasing rate of oxidation of the reduced vanadium ions in the temperature range 573–673°K makes impossible the observation of the first maximum.

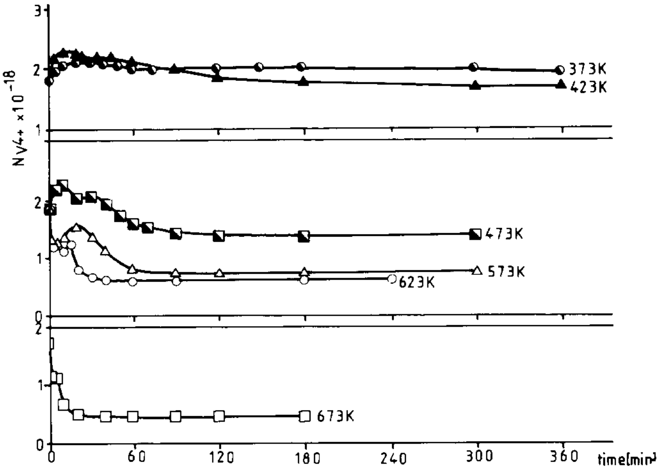

FIG. 1. The change in the number of V^{4+} ions in V_2O_5–MoO_3 catalyst containing 3.4 mole% of MoO_3 in the course of oxygen adsorption, calculated from ESR spectra registered at room temperature.

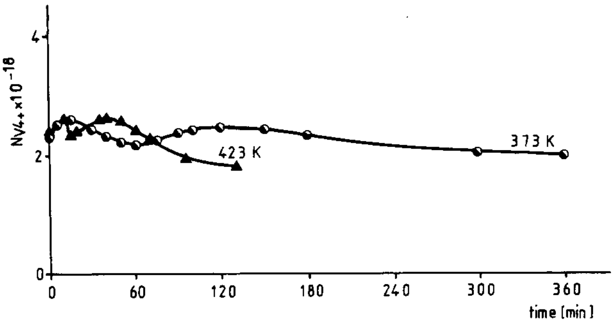

FIG. 2. The change in the number of V^{4+} ions in V_2O_5–MoO_3 catalyst containing 21.0 mole% of MoO_3 in the course of oxygen adsorption, calculated from ESR spectra registered at room temperature.

The number of V^{4+} ions corresponding to the plateau changes with MoO_3 concentration and with temperature in the same way as in the lower temperature range. The number of paramagnetic centers which do not undergo oxidation at a given temperature, represented by the constant level of the plateau, is higher than in the case of partially reduced V_2O_5 (*5*), indicating stabilization of the paramagnetic centers giving the ESR signal in the V_2O_5–MoO_3 catalysts.

3. Kinetics of the Processes Occurring Upon Oxygen Interaction with V_2O_5–MoO_3 Catalysts at Low Temperatures

The kinetic model of the oxidation of partially reduced V_2O_5 proposed by Bielański *et al.* (*5*) assumed that changes in the V^{4+} ion signal intensity, which causes the appearance of a maximum on the curve $N_{V^{4+}} = f(t)$ in the course of oxygen adsorption, may be described by the following set of consecutive reactions:

$$V^{3+} \xrightarrow[k_a]{O_2} V^{4+} \xrightarrow[k_b]{O_2} V^{5+}. \qquad (1)$$

The initial increase of the number of V^{4+} ions is connected with the oxidation of "non-Kramers" V^{3+} ions to V^{4+} ions detectable by ESR. Its subsequent decrease corresponds to the oxidation of the V^{4+} ions to diamagnetic V^{5+} ions. It was shown in Ref. (*5*) that the oxidation processes accompanying chemisorption of oxygen on V_2O_5 in the temperature range 373–473°K

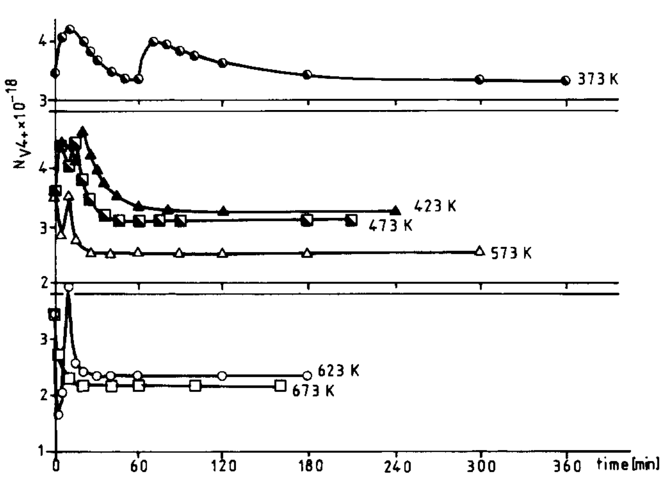

FIG. 3. The change in the number of V^{4+} ions in V_2O_5–MoO_3 catalyst containing 28.0 mole% of MoO_3 in the course of oxygen adsorption, calculated from ESR spectra registered at room temperature.

are restricted to the near-to-surface layers.

The changes of the concentration of paramagnetic centers in the course of chemisorption of oxygen on partially reduced V_2O_5–MoO_3 catalysts at 373–473°K observed in the present work are represented by curves with two maxima (Figs. 1–3). It was now assumed that two sets of consecutive, irreversible reactions which are independent from each other (both of the type of Eq. (1)), occur upon oxygen adsorption. This assumption was justified by the presence in the studied system of two types of paramagnetic center both involving reduced vanadium ions which are stabilized by oxygen vacancies and substitutional Mo^{6+} ions, respectively. The observed changes in the concentration of the paramagnetic centers are of the same order of magnitude as in the case of the oxidation of partially reduced V_2O_5 (*5*). On the other hand, the changes of the signal intensity of partially reduced MoO_3 occurring upon oxygen interaction are negligible and no shift of *g* factor toward lower values, characteristic of Mo^{5+} ($g = 1.94$), was observed in the course of oxidation of V_2O_5–MoO_3 catalysts, indicating that the reduced Mo ions do not participate significantly in the observed changes of the ESR spectrum.

The position of the first maximum on curves $N_{V^{4+}}(t)$ is practically independent of MoO_3 concentration which indicates that this maximum, as in partially reduced V_2O_5, is a result of the following reactions

$$V^{3+}_{(1)} \xrightarrow[k_{A(1)}]{O_2} V^{4+}_{(1)} \xrightarrow[k_{B(1)}]{O_2} V^{5+}_{(1)} \tag{2}$$

involving vanadium ions stabilized by oxygen vacancies.

On the other hand, the position of the second maximum depends on MoO_3 concentration. Therefore, it may be concluded that this maximum is a result of:

$$V^{3+}_{(2)} \xrightarrow[k_{A(2)}]{O_2} V^{4+}_{(2)} \xrightarrow[k_{B(2)}]{O_2} V^{5+}_{(2)} \tag{3}$$

in which $V^{3+}_{(2)}$ and $V^{4+}_{(2)}$ ions stabilized in the vicinity of substitutional Mo^{6+} ions are engaged.

It was assumed that the above reactions are of first order with respect to the vanadium ion concentration. All the experiments were carried out under a constant pressure of oxygen and thus the following kinetic equations expressing the rate of change of the vanadium ion concentration may be written

$$\frac{dN_{V^{3+}_{(1)}}}{dt} = -k_{A(1)} \cdot N_{V^{3+}_{(1)}}, \tag{4}$$

$$\frac{dN_{V^{4+}_{(1)}}}{dt} = k_{A(1)} \cdot N_{V^{3+}_{(1)}} - k_{B(1)} \cdot \mathrm{N}_{V^{4+}_{(1)}}, \tag{5}$$

$$\frac{dN_{V^{5+}_{(1)}}}{dt} = k_{B(1)} \cdot N_{V^{4+}_{(1)}}, \tag{6}$$

$$\frac{dN_{V^{3+}_{(2)}}}{dt} = -\,k_{A(2)} \cdot N_{V^{3+}_{(2)}}, \tag{7}$$

$$\frac{dN_{V^{4+}_{(2)}}}{dt} = k_{A(2)} \cdot N_{V^{3+}_{(2)}} - k_{B(2)} \cdot \mathrm{N}_{V^{4+}_{(2)}}, \tag{8}$$

$$\frac{dN_{V^{5+}_{(2)}}}{dt} = k_{B(2)} \cdot N_{V^{4+}_{(2)}}. \tag{9}$$

In these equations $N_{V^{n+}_{(i)}}$ denotes the number of vanadium ions at a given oxidation state labeled as "n^+" which are involved in the oxidation process at the moment "*t*." The suffix "*i*" (equal to 1 or 2) indicates processes connected with the first or the second maximum, respectively. The $k_{A(i)}$ and $k_{B(i)}$ are the appropriate rate constants.

As we have stated previously, the reduced molybdenum ions do not contribute to the ESR spectrum of the V_2O_5–MoO_3 catalysts neither before nor in the course of oxygen adsorption. The "non-Kramers" V^{3+} ions are also not detectable by ESR. Thus, from the ESR signal intensity, the total number of V^{4+} ions ($N_{V^{4+}_{total}}(t)$) present in the sample at the moment *t* may be calculated. This value is related to the number of V^{4+} ions stabilized at different sites in V_2O_5–MoO_3 catalysts by

$$N_{V^{4+}_{total}}(t) = N_{V^{4+}_{(1)}}(t) + N_{V^{4+}_{(2)}}(t) + N_{V^{4+}_{bulk}}, \tag{10}$$

where $N_{V^{4+}_{bulk}}$ is the number of V^{4+} ions which at a given temperature do not participate in oxidation.

Unlike partially reduced V_2O_5 where it was possible, on the basis of chemical and ESR data, to calculate the initial concentration of vanadium ions in various oxidation states and also their concentration at a given moment t (5), no such possibility exists in partially reduced vanadia–molybdena catalysts containing reduced vanadium as well as molybdenum ions. Therefore, all the parameters appearing in Eqs. (4)–(10) (rate constants, initial concentrations of reduced vanadium ions, and values of $N_{V^{4+}_{bulk}}$) as well as concentrations of reduced ions after a given time of adsorption were found using a program designed by Łabanowski (*6*), integrating the set of Eqs. (4), (5), (7), and (8) by the 4th order Runge–Kutty–Gill method (*10*). The damped least squares procedure of Meiron (*11*) was applied to fit the parameters to the values of the total number of V^{4+} ions present in the sample at the moment t ($N_{V^{4+}_{total}}(t)$), which was determined from ESR only.

No satisfactory fitting was achieved for the simple model represented by the set of differential Eqs. (4)–(9). The manner in which theoretical curves deviated from experimental ones suggested that upon interaction with oxygen, besides oxidation of reduced vanadium, another process occurs which causes some delay in switching on the reaction: $V^{3+}_{(2)} \rightarrow V^{4+}_{(2)}$. The rates of the processes occurring with some retardation, e.g., those determined by nucleation of new phases or change in the number of centers engaged in a given reaction, are usually approximated by sigmoidal curves with induction periods. We have assumed that the retardation in oxidation of $V^{3+}_{(2)}$ ions is related to the change with time of the number of these ions accessible for oxidation, which may be described by a function of sigmoidal shape. We have thus modified Eqs. (7) and (8) by a function: $F(t) = 0.5\,\{1 + \mathrm{erf}\,[a(t - t_s)]\}$ where $\mathrm{erf}(u) = (2/\sqrt{\pi})\int_0^u e^{-x^2}\,dx$ is an error function with variable u equal to $a(t - t_s)$, the parameter t_s indicates the point of inflection of the sigmoidal curve $F(t)$ and the parameter a determines the rate of increase of the function $F(t)$. The modified Eqs. (7) and (8) have the following form:

$$\frac{dN_{V^{3+}_{(2)}}}{dt} = -\,k_{A(2)} \cdot N_{V^{3+}_{(2)}} \cdot 0.5\,\{1 + \mathrm{erf}[a(t - t_s)]\}, \qquad (7a)$$

$$\frac{dN_{V^{4+}_{(2)}}}{dt} = k_{A(2)} \cdot N_{V^{3+}_{(2)}} \cdot 0.5\,\{1 + \mathrm{erf}[a(t - t_s)]\} - k_{B(2)} \cdot N_{V^{4+}_{(2)}}. \qquad (8a)$$

Figures 4–6 present the fitting of the theo-

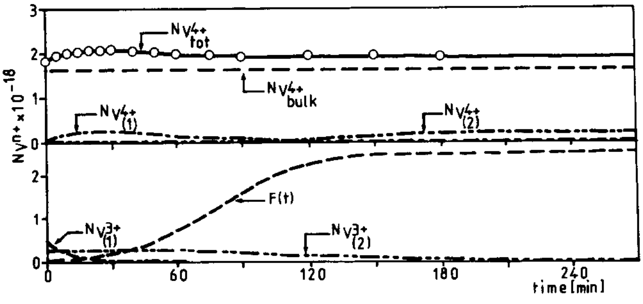

FIG. 4. The fitting of the theoretical kinetic curve $N_{V^{4+}_{tot}}(t)$ (solid line) to experimental data (circles) for oxygen adsorption at 373°K on V_2O_5–MoO_3 catalyst containing 3.4 mole% of MoO_3. The changes of $N_{V^{4+}_{(1)}}$, $N_{V^{4+}_{(2)}}$, $N_{V^{3+}_{(1)}}$, $N_{V^{3+}_{(2)}}$, and $F(t)$ with time of adsorption as well as the value of $N_{V^{4+}_{bulk}}$ are calculated from kinetic equations (see text).

TABLE 3

Numbers of Reduced Vanadium Ions Calculated from Kinetic Equations

Parameter	Temp (°K)	V_2O_5–MoO_3		
		3.4 mole% MoO_3	21.0 mole% MoO_3	28.0 mole% MoO_3
$N_{V_{(1)}^{3+}}(O)$	373	0.39×10^{18}	1.03×10^{18}	2.03×10^{18}
	423	0.88×10^{18}	1.34×10^{18}	2.86×10^{18}
	473	1.20×10^{18}	—	3.05×10^{18}
$N_{V_{(1)}^{4+}}(O)$	373	0.04×10^{18}	0.29×10^{18}	0.17×10^{18}
	423	0.05×10^{18}	0.50×10^{18}	0.29×10^{18}
	473	0.08×10^{18}	—	0.38×10^{18}
$N_{V_{(2)}^{3+}}(O)$	373	0.29×10^{18}	1.27×10^{18}	0.78×10^{18}
	423	0.41×10^{18}	2.17×10^{18}	0.97×10^{18}
	473	0.60×10^{18}	—	1.01×10^{18}
$N_{V_{(2)}^{4+}}(O)$	373	0.09×10^{18}	0.13×10^{18}	0.01×10^{17}
	423	0.14×10^{18}	0.17×10^{18}	0.01×10^{17}
	473	0.28×10^{18}	—	0.01×10^{17}
$N_{V_{bulk}^{4+}}$	373	1.68×10^{18}	1.91×10^{18}	3.27×10^{18}
	423	1.57×10^{18}	1.70×10^{18}	3.18×10^{18}
	473	1.34×10^{18}	—	3.05×10^{18}

TABLE 4

Kinetic Parameters Calculated from Equations Describing Oxidation of V_2O_5–MoO_3 Catalysts

Parameter[a]	Temp (°K)	V_2O_5–MoO_3		
		3.4 mole% MoO_3	21.0 mole% MoO_3	28.0 mole% MoO_3
$k_{A(1)}$ (min^{-1})	373	0.080	0.062	0.107
	423	0.116	0.084	0.142
	473	0.156	—	0.181
$k_{B(1)}$ (min^{-1})	373	0.014	0.046	0.085
	423	0.032	0.089	0.134
	473	0.057	—	0.190
$k_{A(2)}$ (min^{-1})	373	0.010	0.017	0.479
	423	0.042	0.042	1.032
	473	0.138	—	2.206
$k_{B(2)}$ (min^{-1})	373	0.003	0.013	0.015
	423	0.013	0.044	0.051
	473	0.047	—	0.131
a	373	0.032	0.075	0.248
	423	0.140	0.186	0.736
	473	1.615	—	25.000
t_s (min)	373	78	64	65
	423	28	21	17
	473	23	—	12

[a] The reproducibility of the y values measured was estimated as $y \pm 0.1\,y$.

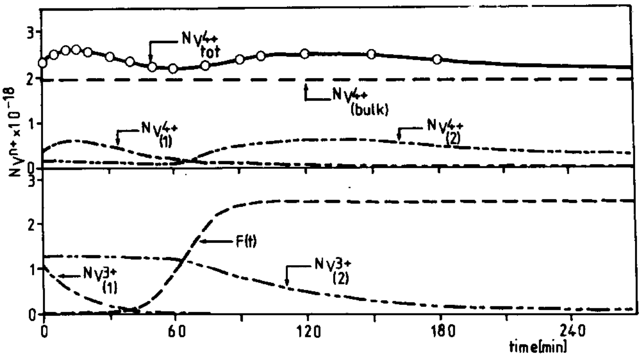

FIG. 5. The fitting of the theoretical kinetic curve $N_{V_{tot}^{4+}}(t)$ (solid line) to experimental data (circles) for oxygen adsorption at 373°K on V_2O_5–MoO_3 catalyst containing 21.0 mole% of MoO_3. The changes of $N_{V_{(1)}^{4+}}$, $N_{V_{(2)}^{4+}}$, $N_{V_{(1)}^{3+}}$, $N_{V_{(2)}^{3+}}$, and $F(t)$ with time of adsorption as well as the value of $N_{V_{bulk}^{4+}}$ are calculated from kinetic equations.

retical curves found by numerical integration of Eqs. (4), (5), (7a), and (8a) to the experimental data obtained at 373°K. Equally good fit was obtained for temperatures 423 and 473°K. Figures 4–6 show also the calculated changes of concentration of particular reduced vanadium ions in the course of adsorption and the time dependence of the function $F(t)$ modulating Eqs. (7a) and (8a). The values of the parameters calculated from the kinetic equations are given in Tables 3 and 4. It should be mentioned that the fitting of the kinetic model to the experimental data and calculations of the kinetic parameters are based on the change of only a small portion of the reduced vanadium ions. The reproducibility of these parameters determined for two or three sets of the experiments performed at the same conditions was within 20% of the measured value. The physical sense of the kinetic parameters will be discussed later in connection with a model based on the assumption that the number of $V_{(2)}^{3+}$ ions accessible for oxidation is a function of time.

4. *Kinetic Parameters of the Oxidation Processes*

The numbers of reduced vanadium ions accessible for oxidation at a given tempera-

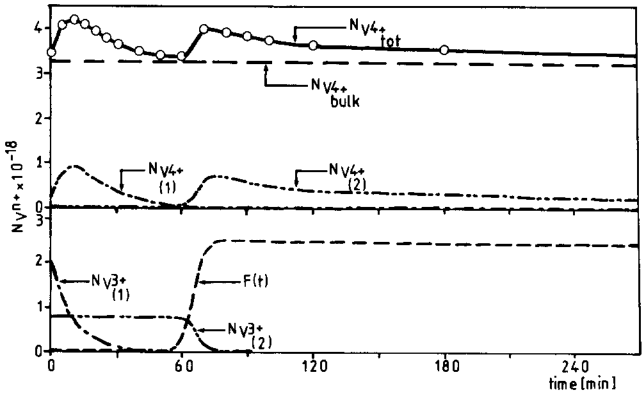

FIG. 6. The fitting of the theoretical kinetic curve $N_{V_{tot}^{4+}}(t)$ (solid line) to experimental data (circles) for oxygen adsorption at 373°K on V_2O_5–MoO_3 catalyst containing 28.0 mole% of MoO_3. The changes of $N_{V_{(1)}^{4+}}$, $N_{V_{(2)}^{4+}}$, $N_{V_{(1)}^{3+}}$, $N_{V_{(2)}^{3+}}$, and $F(t)$ with time of adsorption as well as the value of $N_{V_{bulk}^{4+}}$ are calculated from kinetic equations.

ture represented by the values $N_{V_{(i)}^{n+}}(O)$ are given in Table 3. The amount of these ions changes with concentration of molybdenum in a manner dependent on the type of their stabilization. The total number of vanadium ions, stabilized by oxygen vacancies, which undergo oxidation ($N_{V_{(1)}^{3+}}(O) + N_{V_{(1)}^{4+}}(O)$) increases constantly with molybdenum content, similarly to the total reduction degree of the catalyst. On the other hand, the number of vanadium ions stabilized by Mo^{6+} is the highest for the catalyst containing 21.0 mole% of MoO_3. The latter effect will be commented on later in connection with the processes accompanying oxidation of these ions (Section 5).

The amount of V^{4+} ions which do not take part in oxidation, represented by the value $N_{V_{bulk}^{4+}}$, increases with increasing content of molybdenum in parallel with the increase of the total reduction degree of the catalyst (Table 2). The value of $N_{V_{bulk}^{4+}}$ diminishes with increasing temperature. The amount of reduced vanadium engaged in oxidation increases simultaneously. In this respect, the V_2O_5–MoO_3 catalysts differ from the partially reduced V_2O_5 for which, in the temperature range 373–473°K, the number of vanadium ions taking part in oxidation is constant. This effect seems to indicate that in the studied system, in the above-mentioned temperature range, diffusion processes occur which cause the number of reduced vanadium ions accessible for oxidation to change with time.

The amount of metal ions which were oxidized after a given time of adsorption, calculated from kinetic equations, may be compared with that determined from chemical analysis and ESR (Table 5). The number of reduced vanadium and molybdenum ions present in the catalyst but not detectable by ESR was calculated as being equal to the difference between the data from chemical analysis and ESR (Table 5, column 5). Subtracting the number of these ions present in the sample after 300 min of adsorption from their initial number, the amount of vanadium and molybdenum ions not detectable by ESR which were oxidized in the course of adsorption may be found (see column 6). For comparison with these data, the number of V^{3+} ions oxidized after the same time of adsorption, calculated from the kinetic equations, is given in column 7. The difference between the values obtained from chemical analysis and ESR (column 6) and those calculated from the kinetic equations (column 7) is presented in column 8. In the case of the catalyst containing 3.4 mole% of MoO_3, the difference is very small indicating that the amount of reduced metal ions not detectable by ESR, other than V^{3+}, is negligible. This difference increases with increasing content of MoO_3 in catalyst which may be explained, in agreement with the Raman spectra, by the presence of Mo^{4+} ions. The reasonable result of the above calculations based on the values obtained in two independent ways seems to support the assumed kinetic model.

The reasonable agreement found between the number of V^{4+} ions not engaged in oxidation at a given temperature ($N_{V_{bulk}^{4+}}$), calculated from the kinetic equations (Table 3), and the value of V^{4+} ions corresponding to the plateau on the $N_{V^{4+}}(t)$ curve (Figs. 1–3) is further evidence supporting the kinetic model.

The values of the rate constants of the reactions in which vanadium ions stabilized by oxygen vacancies are engaged (Table 4) are higher than the appropriate rate constants for partially reduced V_2O_5 (*5*). Taking into account that the activation energies are similar in both cases (Table 6 and Ref. (*5*)), the conclusion may be drawn that this difference is related to different values of the preexponential factor. Evidently, higher nonstoichiometry and inhomogeneity of partially reduced V_2O_5–MoO_3 catalysts, as compared with partially reduced V_2O_5, offer more possibilities for oxygen adsorption on crystal defects and phase boundaries, thus increasing the probability of effective collisions of the reagents.

The equalization of appropriate $k_{A(1)}$ and

TABLE 5

Comparison of the Experimentally Determined Numbers of Reduced Vanadium and Molybdenum Ions in V_2O_5–MoO_3 Catalysts with those Calculated from Kinetic Equations[a]

Temp. (°K)	Time of adsorption (min)	Number of reduced vanadium and molybdenum ions[b] ($\times 10^{18}$)	Number of V^{4+} ions[c] ($\times 10^{18}$)	Number of V^{3+} and Mo^{4+} ions[d] ($\times 10^{18}$)	Number of V^{3+} and Mo^{4+} ions oxidized in the course of adsorption[e] ($\times 10^{18}$)	Number of $V^{3+}_{(1)}$ and $V^{3+}_{(2)}$ ions oxidized in the course of adsorption[f] ($\times 10^{18}$)	Number of reduced molybdenum ions oxidized in the course of adsorption[g] ($\times 10^{18}$)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
				V_2O_5–MoO_3 (3.4 mole% MoO_3)			
373	0	11.74	1.81	9.93	0	0	0
	300	10.36	1.90	8.46	1.47	1.30	0.17
423	0	11.74	1.76	9.98	0	0	0
	300	8.91	1.59	7.32	2.66	2.58	0.08
473	0	11.74	1.71	10.03	0	0	0
	300	7.69	1.35	6.34	3.69	3.60	0.09
				V_2O_5–MoO_3 (21.0 mole% MoO_3)			
373	0	18.31	2.34	15.97	0	0	0
	300	12.83	2.06	10.77	5.20	4.56	0.64
				V_2O_5–MoO_3 (28.0 mole% MoO_3)			
373	0	20.78	3.45	17.33	0	0	0
	300	14.03	3.38	10.65	6.68	5.62	1.06
423	0	20.78	3.48	17.30	0	0	0
	300	11.38	3.18	8.21	9.09	7.66	1.42
473	0	20.66	3.43	17.33	0	0	0
	300	10.36	3.04	7.32	10.01	8.12	1.90

[a] Total number of V and Mo atoms in the sample 100.0 ± 0.8 × 10^{18}. 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.

[b] $y = (N_{V^{4+}} + 2N_{V^{3+}} + 2N_{Mo^{4+}}) \pm 2s_1$ (from chemical analysis), $2s_1 = 0.10 \times 10^{18}$.

[c] $y = (N_{V^{4+}}) \pm 2s_2$ (from ESR), $2s_2 = 0.06 \times 10^{18}$.

[d] $y = (2N_{V^{3+}} + 2N_{Mo^{4+}}) \pm 2s_3$ (column 3 − column 4). $2s_3 = 0.10 \times 10^{18}$.

[e] $y = \Delta(2N_{V^{3+}} + 2N_{Mo^{4+}}) \pm 2s_3$; $2s_3 = 0.10 \times 10^{18}$.

[f] $2N_{V^{3+}_{(1)}} + 2N_{V^{3+}_{(2)}}$ (from kinetic equation).

[g] $y = (\Delta 2N_{Mo^{4+}}) \pm 2s_3$ (column 6 − column 7). $2s_3 = 0.10 \times 10^{18}$.

TABLE 6

Activation Energies of the Oxidation Processes Occurring in V_2O_5–MoO_3 Catalysts in the Temperature Range 373–473°K[a]

Reaction	Activation energy (kJ mole^{-1})		
	(3.4 mole% MoO_3)	(21.0 mole% MoO_3)	(28.0 mole% MoO_3)
$V^{3+}_{(1)} \xrightarrow[k_{A(1)}]{} V^{4+}_{(1)}$	9.7	7.8	7.7
$V^{4+}_{(1)} \xrightarrow[k_{B(1)}]{} V^{5+}_{(1)}$	20.8	17.4	11.6
$V^{3+}_{(2)} \xrightarrow[k_{A(2)}]{} V^{4+}_{(2)}$	37.6	22.9	22.2
$V^{4+}_{(2)} \xrightarrow[k_{B(2)}]{} V^{5+}_{(2)}$	41.0	30.7	31.0

[a] The reproducibility of the y values measured was estimated as $y \pm 0.1\,y$.

$k_{B(1)}$ constants with increasing MoO_3 content indicates that also the process of oxidation of reduced vanadium stabilized by oxygen vacancies is influenced by the presence of molybdenum.

As already mentioned, the activation energies of the two stages of oxidation,

$$V^{3+}_{(1)} \xrightarrow[k_{A(1)}]{O_2} V^{4+}_{(1)} \xrightarrow[k_{B(1)}]{O_2} V^{5+}_{(1)}$$

(Table 6) agree well with the values found by Bielanski *et al.* (*5*) for the oxidation of vanadium ions in partially reduced V_2O_5. This fact is consistent with the assumption that the oxidation of reduced vanadium stabilized by oxygen vacancies is responsible for the appearance of the first maximum on the kinetic curves. On the other hand, the activation energies of the reactions

$$V^{3+}_{(2)} \xrightarrow[k_{A(2)}]{O_2} V^{4+}_{(2)} \xrightarrow[k_{B(2)}]{O_2} V^{5+}_{(2)}$$

responsible for the appearance of the second maximum, are much greater (Table 6). Hence, a different mechanism for both reactions and better stabilization of reduced vanadium in the vicinity of Mo^{6+} ions than in the vicinity of oxygen vacancies may be concluded.

The values of the activation energy of the reactions $V^{3+}_{(1)} \rightarrow V^{4+}_{(1)}$ and $V^{3+}_{(2)} \rightarrow V^{4+}_{(2)}$ are lower than those of the reactions $V^{4+}_{(1)} \rightarrow V^{5+}_{(1)}$ and $V^{4+}_{(2)} \rightarrow V^{5+}_{(2)}$, respectively, indicating high activity of V^{3+} centers in the oxidation process. The highest value of activation energy and the lowest value of rate constant found for the process $V^{4+}_{(2)} \rightarrow V^{5+}_{(2)}$ (Tables 4 and 6) may serve as an evidence of effective stabilization of the V^{4+} in the phase of the solid solution V_2O_5–MoO_3.

5. *Physical Model of the Oxidation Processes*

X-Ray analysis revealed the presence of V_2O_5–MoO_3 solid solution and the MoO_3 phase in the catalysts. In the course of the thermal decomposition of the precursors of the catalysts, followed by heat treatment *in vacuo*, reduction of the particular phases occurs. Simultaneously, the surface layers of the solid solution become enriched with reduced molybdenum (*1–4*). On the surface of the catalyst, the reduced vanadium ions are stabilized mainly by oxygen vacancies, whereas in the near-to-surface layers (which are less reduced but still enriched with molybdenum) these ions may be stabilized by oxygen vacancies as well as by Mo^{6+}.

Upon interaction with oxygen at 373–473°K, the V^{3+} and V^{4+} ions stabilized by oxygen vacancies are oxidized giving rise to the appearance of the first maximum on the kinetic curves. Simultaneously, oxidation of the reduced molybdenum occurs which may be detected only by chemical analysis because, as shown in our preliminary experiments, the changes in the oxidation state of molybdenum are not reflected in the ESR spectra. In the course of oxidation, the diffusion of reduced vanadium ions from deeper layers of the catalyst to the surface layers enriched with molybdenum occurs. Due to the diffusion processes, the relative concentration of molybdenum in the surface layers of the catalyst continuously decreases. After a certain period of time it becomes too low to stabilize effectively the reduced vanadium ions, especially the V^{3+} ions which require twice the number of Mo^{6+} in their vicinity to ensure electroneutrality of the lattice. Oxygen may then attack the V^{3+} ions in the solid solution and on the kinetic curve the second maximum appears. With increasing content of MoO_3 in the catalyst, the delay in oxidizing of vanadium ions stabilized by Mo^{6+} should thus increase.

In the kinetic model the retardation in oxidation of V^{3+} ions in the phase of the solid solution is described by modulation of the Eqs. (7) and (8) by a function of sigmoidal shape with a period of induction dependent on the concentration of MoO_3 (Figs. 4–6). At the beginning of adsorption, the rate of oxidation of the $V^{3+}_{(2)}$ ions is practically equal to zero which may be interpreted as a result of the lack of these ions accessible for oxidation. Thus, at this moment oxygen reacts only with reduced vanadium and with molybdenum stabilized by oxygen vacancies. The delay in oxidizing of $V^{3+}_{(2)}$ ions is evidently dependent on the content of molybdena. Indeed, in the catalyst containing small amounts of MoO_3, the reaction $V^{3+}_{(2)} \rightarrow V^{4+}_{(2)}$ is switched on practically at the moment when chemisorption is initiated (Fig. 4) whereas in catalysts richer with MoO_3 the delay of this reaction increases (Figs. 5 and 6).

The rate of the process leading to exposure of $V^{3+}_{(2)}$ ions for oxidation may be described by parameter a. At a given temperature, the parameter a increases with increasing MoO_3 content. The enrichment of the surface layers of the solid solution of MoO_3 in V_2O_5 with molybdenum results in an increase of the concentration gradient of reduced vanadium ions directed from the deeper surface layers to the surface. This latter factor may cause an increase of the diffusion rate of vanadium ions toward the surface, which is reflected in the high value of parameter a. The increase of the diffusion rate of vanadium ions may also be connected with lability of the lattice due to the higher concentration of defects in catalysts with high content of MoO_3. It is worthwhile to note that the parameter a attains its maximum value in the catalyst containing 28.0 mole% of MoO_3. In spite of that, the number of vanadium ions accessible for oxidation, stabilized by Mo^{6+} ions, is lower than in the catalyst containing 21.0 mole% of MoO_3 (Table 3). These two facts indicate that in the catalyst richest with molybdenum the segregation process may lead to blocking of the surface by molybdenum.

In the above considerations, the physical sense of the diffusion rate constant of vanadium ions was attributed to parameter a which characterizes the rate of exposure of V^{3+} ions to oxidation in partially reduced V_2O_5–MoO_3 catalysts. The Arrhenius plots of this parameter are not straight lines but consist of two intersecting segments. In the temperature range 373–423°K, the estimated values of the activation energy amount to about 30 kJ $mole^{-1}$ for all the catalysts, whereas in the temperature range 423–473°K they vary with increasing MoO_3 content from 80 to 120 kJ $mole^{-1}$. Realizing that the obtained values represent only a very rough estimation, they may be compared with the value of the activation energy of diffusion occurring in the bulk of partially reduced V_2O_5 at temperatures exceeding 473°K, which is equal to 126 kJ $mole^{-1}$ (*5*). In the temperature range 423–473°K the value ascribed by us to the apparent activation energy of the diffusion process in the catalysts containing molybdena does not differ very strongly from that characteristic of the diffusion in the bulk of

V_2O_5, indicating that the vanadium ions from the bulk of the vanadia–molybdena catalysts are engaged in oxidation also at relatively low temperatures. This effect may originate in the increasing number of diffusion paths due to the higher inhomogeneity and nonstoichiometry of V_2O_5–MoO_3 catalysts as compared with V_2O_5.

CONCLUSIONS

Two different paramagnetic centers involving V^{4+} ions, stabilized by oxygen vacancies and substitutional Mo^{6+} ions, respectively, have been found in strongly defective heterogeneous vanadia–molybdena catalysts. It is concluded from adsorption experiments that V^{4+} ions stabilized by anion vacancies are more active in oxidation processes than V^{4+} centers situated in the vicinity of substitutional Mo^{6+} ions. It may be supposed that the presence of these latter ions ensures a higher selectivity of the vanadia–molybdena catalysts in the reactions of oxidation of hydrocarbons as compared with catalysts based on pure V_2O_5.

The V^{3+} ions and reduced molybdenum ions not detectable by ESR contribute also to the high reduction degree of V_2O_5–MoO_3 catalysts. Similarly to the case of V^{4+} centers, the V^{3+} ions stabilized in the vicinity of Mo^{6+} are less active in the oxidation processes than those stabilized by oxygen vacancies. On the other hand, both types of V^{3+} ions are more easily oxidized than the respective V^{4+} centers.

It is suggested that the kinetics of catalyst oxidation is influenced by the segregation processes occurring in the course of the redox treatment.

ACKNOWLEDGMENTS

The authors are greatly indebted to Professor A. Bielański for helpful discussions and to Dr. J. Łabanowski of the Institute of Molecular Biology of the Jagiellonian University for elaboration of the programs and computing of the ESR data. The performing of TG, DTA, and chemical analyses, as well as the measuring of Raman spectra, were carried out in the Central Laboratory for Physicochemical Analyses and Structural Investigations, Kraków, Poland, and are gratefully acknowledged.

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