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

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A kinetic model based on two sets of consecutive reactions involving V^{5+} and V^{4+} ions situated at different sites in the lattice was proposed for the reduction of V_2O_5–MoO_3 catalysts occurring upon interaction with propylene at 373 K. The role of temperature in the involvement of the ions from the surface layers and from the bulk of the catalysts in the reduction has been discussed. The dependence of the delay in reduction of vanadium on the segregation processes was considered.

INTRODUCTION

In order to obtain a better understanding of the behavior of mixed vanadia–molybdena catalysts in catalytic oxidation of hydrocarbons we have studied redox processes occurring in the course of adsorption of oxygen (*1*) and propylene. It was found previously (*2–5*) that the oxidation process is associated with a segregation of metal ions leading to enrichment of the surface layers of the V_2O_5–MoO_3 catalyst with vanadium. On the other hand, the interaction of these catalysts with propylene, consisting in the removal of oxygen from the lattice, should lead to enrichment of the surface layers with molybdenum.

In the previous work with V_2O_5–MoO_3 (*1*) we described two different types of paramagnetic centers, involving V^{4+} ions stabilized by oxygen vacancies and substitutional Mo^{6+} ions. We also postulated the existence of two types of V^{3+} ions. It was concluded that the ions stabilized by Mo^{6+} (both V^{4+} and V^{3+}) are less active in the oxidation process than those stabilized in the vicinity of oxygen vacancies.

In the present work the kinetics of the reduction of the vanadia–molybdena system upon interaction with propylene was investigated by means of ESR and chemical analysis in order to test the proposed model of the redox processes (*1*).

EXPERIMENTAL

Materials. V_2O_5–MoO_3 catalysts with MoO_3 contents of 3.4, 21.0, and 28.0 mol% were obtained by thermal decomposition *in vacuo* (10^{-3}–10^{-4} Pa) at 623 K of mixtures of NH_4VO_3 (pure, Reachim USSR) and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (anal.pure, POCh, Poland). The detailed procedure was described in Ref. (*1*).

Chemical analysis. The degree of reduction of the catalysts was determined using $KMnO_4$. The samples were dissolved in a small amount of H_2SO_4 (1 : 1) in the absence of air (in a stream of purified nitrogen) and then titrated with $KMnO_4$ (*1*). The results are given in Table 1. 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 (Technical University, Wrocław). The g factors were determined using DPPH as a standard. Polycrystalline $VOSO_4$, with ESR parameters similar to those of partially reduced V_2O_5–MoO_3 catalysts, was used as a stan-

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TABLE 1

Comparison of the Experimentally Determined Numbers of Vanadium and Molybdenum Ions Reduced in the Course of Propylene Adsorption at 373 K with Those Calculated from Kinetic Equations[a]

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^{4+} ions created in the course of reduction[e] ($\times 10^{18}$)	Number of V^{3+} ions created in the course of reduction[f] ($\times 10^{18}$)	Number of V^{5+} ions reduced in the course of adsorption[g] ($\times 10^{18}$)	Number of $V^{5+}_{(1)}$ and $V^{5+}_{(2)}$ ions reduced in the course of adsorption[h] ($\times 10^{18}$)	Number of Mo^{4+} ions created by reduction of Mo^{6+} [i] ($\times 10^{18}$)
1	2	3	4	5	6	7	8	9
V_2O_5–MoO_3 (3.4 mol% MoO_3)								
0	11.4 ± 0.1	1.84 ± 0.05	4.8 ± 0.1	0	0	0	0	0
10	14.8 ± 0.1	3.35 ± 0.09	5.7 ± 0.2	1.51 ± 0.09	0.9 ± 0.2	2.4 ± 0.2	2.1	0.3 ± 0.2
20	17.2 ± 0.1	3.53 ± 0.09	6.8 ± 0.2	1.69 ± 0.09	2.0 ± 0.2	3.7 ± 0.2	3.3	0.4 ± 0.2
30	18.8 ± 0.2	3.24 ± 0.09	7.8 ± 0.2	1.40 ± 0.09	3.0 ± 0.2	4.4 ± 0.2	4.0	0.4 ± 0.2
60	22.5 ± 0.2	3.10 ± 0.08	9.7 ± 0.3	1.26 ± 0.08	4.9 ± 0.3	6.2 ± 0.3	5.7	0.5 ± 0.3
300	28.3 ± 0.2	2.03 ± 0.05	13.1 ± 0.4	0.19 ± 0.05	8.3 ± 0.4	8.5 ± 0.4	8.1	0.4 ± 0.4
V_2O_5–MoO_3 (21.0 mol% MoO_3)								
0	18.3 ± 0.2	2.63 ± 0.07	7.8 ± 0.2	0	0	0	0	0
180	31.7 ± 0.3	2.15 ± 0.06	14.8 ± 0.4	−0.48 ± 0.07	7.0 ± 0.4	6.5 ± 0.4	5.7	0.8 ± 0.4
V_2O_5–MoO_3 (28.0 mol% MoO_3)								
0	20.5 ± 0.2	3.37 ± 0.09	8.6 ± 0.2	0	0	0	0	0
10	24.9 ± 0.2	4.1 ± 0.1	10.4 ± 0.3	0.7 ± 0.1	1.8 ± 0.3	2.5 ± 0.3	1.7	0.8 ± 0.3
20	27.0 ± 0.2	3.9 ± 0.1	11.5 ± 0.3	0.5 ± 0.1	2.9 ± 0.3	3.4 ± 0.3	2.3	1.1 ± 0.3
30	27.9 ± 0.2	3.6 ± 0.1	12.1 ± 0.3	0.2 ± 0.1	3.5 ± 0.3	3.7 ± 0.3	2.7	1.0 ± 0.3
60	30.4 ± 0.3	3.8 ± 0.1	13.3 ± 0.4	0.4 ± 0.1	4.7 ± 0.4	5.1 ± 0.4	3.8	1.3 ± 0.4
180	31.1 ± 0.3	3.09 ± 0.08	14.0 ± 0.4	−0.3 ± 0.09	5.4 ± 0.4	5.1 ± 0.4	3.8	1.3 ± 0.4

[a] Total number of V and Mo atoms in the sample = 10^{20}. The confidence interval of the measured value $y \pm 2s$ (s, standard deviation) corresponds to 0.95 probability level.

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

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

[d] $y = (N_{V^{3+}} + N_{Mo^{4+}}) \pm 2s_3 \left(\frac{\text{column 2} - \text{column 3}}{2}\right)$.

[e] $y = (N_{V^{4+}}) \pm 2s_2$.

[f] $y = (N_{V^{3+}}) \pm 2s_3$.

[g] $y = N_{V^{4+}} + N_{V^{3+}}) \pm 2s_3$ (column 5 + column 6).

[h] $y = (N_{V^{5+}_{(1)}} + N_{V^{5+}_{(2)}})$ (from kinetic equations).

[i] $y = (N_{Mo^{4+}}) \pm 2s_3$ (column 7 − column 8).

dard of spin concentration. The same procedure of the integration of ESR spectra was applied as in Ref. (*1*). The samples showed a room temperature ESR signal with $g = 1.960 \pm 0.005$, which is characteristic of V^{4+} ions stabilized by oxygen vacancies in reduced V_2O_5 (*6*). The number of V^{4+} paramagnetic centers determined from the integrated intensity of the ESR signal changed with increase of MoO_3 content in the range 1.8–3.4 × 10^{18} per sample containing 10^{20} atoms of V and Mo (Table 1). The number was always smaller than the number of reduced vanadium and molybdenum ions calculated from chemical analysis due to the presence of the "non-Kramers" V^{3+} and Mo^{4+} ions which are not detectable by ESR (*1*). The formation of V^{4+}–V^{4+} and/or V^{4+}–Mo^{5+} pairs, not visible by ESR, during reduction *in vacuo* and also during propylene reduction at 373 K, may be neglected considering the temperature dependence of the signal intensity, similarly as in Ref. (*1*). The relative standard deviation $(s_2/y) \times 100$ of the determination of the number of spins in partially reduced samples, averaged over the y values measured, amounted to 1.3%. In the calculations

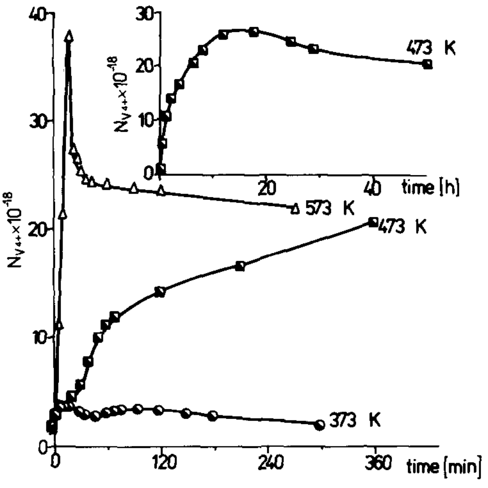

FIG. 1. The change in the number of V^{4+} ions in V_2O_5–MoO_3 containing 3.4 mol% MoO_3 in the course of propylene adsorption, calculated from ESR spectra registered at room temperature.

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%.

Propylene adsorption. Pure propylene (99.9% from Factory of Nitrogen Compounds, Plock, Poland) was used for the adsorption which was carried out in the temperature range of 373–573 K at a pressure of 10 kPa. Propylene was introduced into ampoules containing the partially reduced samples, which were subsequently heated at a given temperature for a certain period of time. The consumption of propylene was negligible in comparison to the total amount of introduced gas. After rapidly cooling the samples to room temperature, the ESR spectrum was measured and then the procedure of heating was repeated until a constant ESR signal intensity was reached. The samples destined for chemical analysis were treated exactly in the same way.

RESULTS AND DISCUSSION

1. Adsorption of Propylene

The curves describing changes of the ESR signal intensity in the course of interaction of V_2O_5–MoO_3 catalysts with propylene at 373 K passed through two maxima and after a certain period of time achieved a constant level [Figs. 1–3]. The position of the first maximum was practically independent of the molybdenum concentration whereas the second maximum shifted with increasing amount of MoO_3 toward shorter adsorption time. Both maxima were rather flat, and the level at which the curves $N_{V^{4+}}$ (t) (where $N_{V^{4+}}$ is number of V^{4+} ions in the sample at time t) were stabilized after passing the maxima was similar to that prior to propylene adsorption. It was shown previously (*1*, *6*) that the height of this level is related to the number of paramagnetic centers not involved in the redox processes. It may therefore be assumed that at 373 K only a small number of paramagnetic centers, i.e., only those situated on the surface or in the near-to-surface layers, is involved in the reduction.

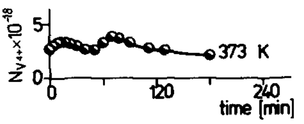

FIG. 2. The change in the number of V^{4+} ions in V_2O_5–MoO_3 containing 21.0 mol% MoO_3 in the course of propylene adsorption, calculated from ESR spectra registered at room temperature.

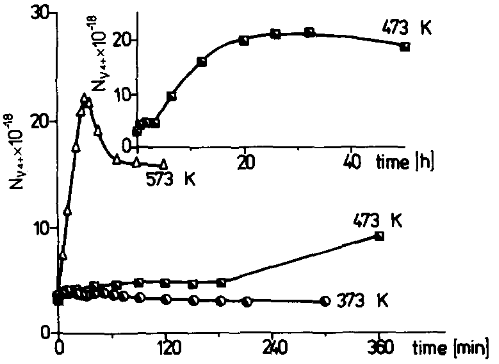

FIG. 3. The change in the number of V^{4+} ions in V_2O_5–MoO_3 containing 28.0 mol% MoO_3 in the course of propylene adsorption, calculated from ESR spectra registered at room temperature.

The character of the kinetic curves changed with increase of the temperature. At 473 K two maxima were still present but the second one was much higher than that formed at the lower temperature. The number of paramagnetic centers related to the second maximum and to the plateau on the $N_{V^{4+}}(t)$ curves corresponded to 20–25% of the total number of vanadium and molybdenum ions present in the samples. Thus it may be concluded that at 473 K the reduction is no longer restricted to the surface layers of the V_2O_5–MoO_3 catalysts but the bulk of the catalyst is also involved. The position of the second maximum shifted toward longer time of propylene adsorption and the height of maximum decreased with increasing molybdenum concentration. After passing the maximum the number of paramagnetic centers decreased very slowly.

An increase of temperature to 573 K led to the appearance of one maximum only on the kinetic curves. The position and height of this maximum changed with MoO_3 concentration similarly to those of the second maximum on kinetic curves describing the reduction process at 473 K.

In the whole range of temperature the number of paramagnetic centers corresponding to the constant level on the curves $N_{V^{4+}}(t)$ was appreciably greater in the V_2O_5–MoO_3 catalysts than in partially reduced V_2O_5 (*6*). The effect may be interpreted as a better stabilization of paramagnetic centers (those giving the ESR signal) in the V_2O_5–MoO_3 system than in the V_2O_5 lattice.

The g value of the ESR signals corresponding to both maxima was characteristic of V^{4+} ions; however, the position of the second maximum changed with MoO_3 concentration. Partially reduced MoO_3 obtained in the same way as V_2O_5–MoO_3 catalysts, i.e., by thermal decomposition of $(NH_4)_6Mo_7O_{24}$, shows two Mo^{5+} signals of very low intensity with g factors below 1.960 (I: $g_x = 1.943$, $g_y = 1.952$, $g_z = 1.879$; II: $g_\perp = 1.930$, $g_\parallel = 1.911$) (*7*). Thus, the appearance of the second maximum cannot be attributed to reduction of molybdenum ions. Therefore, we assume that the changes in the ESR signal intensity of V_2O_5–MoO_3 catalysts occurring in the course of propylene adsorption are connected only with changes in the number of V^{4+} ions. Nevertheless, the presence of molybdenum seems to influence the reducibility of vanadium by propylene.

2. *Kinetics of Reduction at 373 K*

The kinetic model of reduction of the V_2O_5–MoO_3 catalysts elaborated in the present work was based on the assumption that at 373 K propylene may interact only with the centers situated at the surface and in the near-to-surface layers.

Several authors (*8–10*) suggested that the interaction of olefins with V_2O_5 or MoO_3 consists in the oxidation of the hydrocarbons by both surface and bulk oxygen. Removal of oxygen from the surface occurs with simultaneous formation of vanadium and molybdenum ions with lower than +5 and +6 oxidation state, respectively. Subsequently, a reduction of the layers near to the surface (at low temperature) or a bulk reduction (at high temperature) occurs. The removal of oxygen from the lattice of the catalyst is accompanied by a diffusion of cations toward the bulk.

We have postulated that the appearance of two maxima on the reduction curves $N_{V^{4+}}(t)$ was connected with two sets of the following, consecutive reactions:

$$V^{5+}_{(1)} \xrightarrow[k_{A(1)}]{C_3H_6} V^{4+}_{(1)} \xrightarrow[k_{B(1)}]{C_3H_6} V^{3+}_{(1)} \qquad (1)$$

$$V^{5+}_{(2)} \xrightarrow[k_{A(2)}]{C_3H_6} V^{4+}_{(2)} \xrightarrow[k_{B(2)}]{C_3H_6} V^{3+}_{(2)} \qquad (2)$$

where suffixes (1) and (2) denoted the first and the second maximum, respectively.

The initial increase in the intensity of the observed signal is related to the reduction of diamagnetic V^{5+} ions to V^{4+} ions showing the ESR signal. Subsequent reduction of V^{4+} ions to "non-Kramers" V^{3+} ions results in a decrease of the ESR signal intensity. We suppose that in the first set of reactions the $V^{n+}_{(1)}$ vanadium ions situated at the surface of catalyst are engaged, whereas the second set involves the $V^{n+}_{(2)}$ vanadium ions situated in the near-to-surface layers of the V_2O_5–MoO_3 solid solutions. Due to the strong reduction of the surface, the $V^{4+}_{(1)}$ and $V^{3+}_{(1)}$ ions are stabilized mainly by oxygen vacancies, whereas the $V^{4+}_{(2)}$ and $V^{3+}_{(2)}$ ions situated in the near-to-surface layers can be stabilized also in the vicinity of Mo^{6+}. The stabilization of V^{4+} by Mo^{6+} in V_2O_5–MoO_3 catalysts was proved previously (*1*) on the basis of ESR data. Simultaneously with reduction of vanadium the reduction of molybdenum occurs, but, as mentioned earlier, the reduced molybdenum does not contribute to the ESR spectrum of V_2O_5–MoO_3 catalysts and can be detected only by chemical analysis.

We have assumed that two sets of the reactions (1) and (2) are irreversible and independent of each other. Since the experiments of reduction were carried out under constant pressure of propylene, it was also assumed that the reactions (1) and (2) are of zero order with respect to propylene and of first order with respect to the concentration of vanadium ions. The following kinetic equations may be used to describe the rate of changes of the vanadium ions concentration.

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

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

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

$$\frac{dN_{V^{5+}_{(2)}}}{dt} = -k_{A(2)} \cdot N_{V^{5+}_{(2)}} \cdot 0.5\{1 + \mathrm{erf}[a(t - t_s)]\} \tag{6}$$

$$\frac{dN_{V^{4+}_{(2)}}}{dt} = k_{A(2)} \cdot N_{V^{5+}_{(2)}} \cdot 0.5\{1 + \mathrm{erf}[a(t - t_s)]\} - k_{B(2)} \cdot N_{V^{4+}_{(2)}} \tag{7}$$

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

In these equations $N_{V^{n+}_{(i)}}$ denotes the number of vanadium ions at a given oxidation state $n+$ involved in the reduction at time t. Suffix i, equal to 1 or 2, indicates the process connected with the first or the second maximum, respectively. The $k_{A(i)}$ and $k_{B(i)}$ are the corresponding rate constants. The Eqs. (6) and (7) are modified by a sigmoid function, similarly as in Ref. (*1*). The parameters a and t_s denote a rate of increase and an inflection point of the sigmoid curve, respectively. In our model the induction period of the sigmoid curve is interpreted as the period of time necessary for exposure of reaction centers for propylene, whereas the parameter a is the rate of the change of the number of these centers with the reaction time.

The total number of V^{4+} ions $N_{V^{4+}_{\mathrm{total}}}(t)$ present in the sample at the moment t can be calculated from the ESR signal intensity. This value is related to the number of V^{4+} ions situated at the surface $N_{V^{4+}_{(1)}}(t)$ and in the deeper, but still near-to-surface, layers $N_{V^{4+}_{(2)}}(t)$ by the equation

TABLE 2

Number of Reduced Vanadium Ions and Kinetic Parameters Calculated from Equations Describing Reduction of V_2O_5–MoO_3 Catalysts at 373 K[a]

Parameter[b]	V_2O_5–MoO_3 (3.4 mol% MoO_3)	V_2O_5–MoO_3 (21.0 mol% MoO_3)	V_2O_5–MoO_3 (28.0 mol% MoO_3)
$N_{V^{5+}_{(1)}}(0)$	4.89×10^{18}	3.23×10^{18}	2.61×10^{18}
$N_{V^{4+}_{(1)}}(0)$	0.10×10^{18}	0.50×10^{18}	0.40×10^{18}
$N_{V^{5+}_{(2)}}(0)$	3.18×10^{18}	2.48×10^{18}	1.18×10^{18}
$N_{V^{4+}_{(2)}}(0)$	0.27×10^{18}	0.25×10^{18}	0.01×10^{18}
$N_{V^{4+}_{\mathrm{bulk}}}(0)$	1.47×10^{18}	1.87×10^{18}	2.93×10^{18}
$k_{A(1)}$ [min^{-1}]	0.056	0.064	0.096
$k_{B(1)}$ [min^{-1}]	0.056	0.064	0.089
$k_{A(2)}$ [min^{-1}]	0.023	0.320	1.320
$k_{B(2)}$ [min^{-1}]	0.009	0.019	0.017
a	0.340	0.076	0.039
t_s [min]	44	63	65

[a] Total number of V and Mo atoms in the 20- to 30-mg sample = 10^{20}.

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

$$N_{V^{4+}_{total}}(t) = N_{V^{4+}_{(1)}}(t) + N_{V^{4+}_{(2)}}(t) + N_{V^{4+}_{bulk}}, \quad (9)$$

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

The parameters of the differential equations (Eqs. 3–8), i.e., rate constants, initial concentrations of V^{5+} and V^{4+} ions as well as $N_{V^{4+}_{bulk}}$ and also concentrations of these ions after a given time of propylene adsorption, determined as in Ref. (*1*), are given in Table 2. The fitting of the theoretical curves to the experimental data is shown in Figs. 4–6. These figures represent also the changes of concentration of vanadium ions (V^{5+}, V^{4+}) in the course of reduction as well as the time dependence of the sigmoid function $F(t)$.

3. Kinetic Parameters of the Reduction Process

The number of vanadium ions (V^{5+} and V^{4+}) accessible for reduction at 373 K and kinetic parameters of the reduction are summarized in Table 2. The changes of these values with changing MoO_3 concentration will be discussed and the kinetic parameters will be compared with the corresponding parameters found for the oxidation process for which a model of two sets of consecutive reactions $V^{3+}_{(1)} \rightarrow V^{4+}_{(1)} \rightarrow V^{5+}_{(1)}$ and $V^{3+}_{(2)} \rightarrow V^{4+}_{(2)} \rightarrow V^{5+}_{(2)}$ was assumed (*1*).

The total number of V^{5+} ions $N_{V^{5+}_{(1)}}(0) + N_{V^{5+}_{(2)}}(0)$ involved at time $t = 0$ in both sequences of consecutive reactions decreased as the content of MoO_3 increased (Table 2),

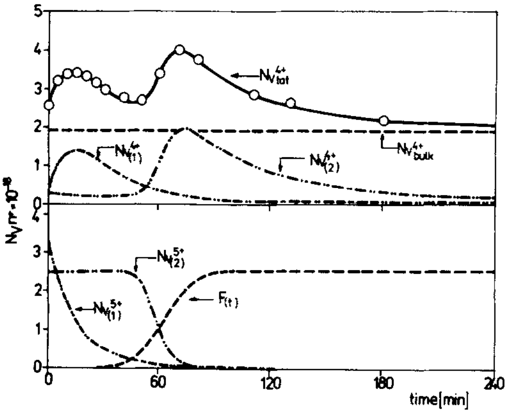

FIG. 5. The fitting of the theoretical kinetic curve $N_{V^{4+}_{tot}}(t)$ (solid line) to experimental data (circles) for propylene adsorption at 373 K on V_2O_5–MoO_3 containing 21.0 mol% MoO_3. The changes of $N_{V^{4+}_{(1)}}$, $N_{V^{4+}_{(2)}}$, $N_{V^{5+}_{(1)}}$, $N_{V^{5+}_{(2)}}$, and $F(t)$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

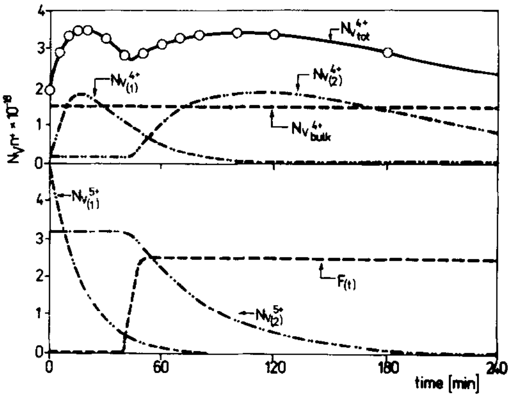

FIG. 4. The fitting of the theoretical kinetic curve $N_{V^{4+}_{tot}}(t)$ (solid line) to experimental data (circles) for propylene adsorption at 373 K on V_2O_5–MoO_3 containing 3.4 mol% MoO_3. The changes of $N_{V^{4+}_{(1)}}$, $N_{V^{4+}_{(2)}}$, $N_{V^{5+}_{(1)}}$, $N_{V^{5+}_{(2)}}$, and $F(t)$ with time of adsorption as well as the value of $N_{V^{4+}_{bulk}}$ are calculated from kinetic equations (see text).

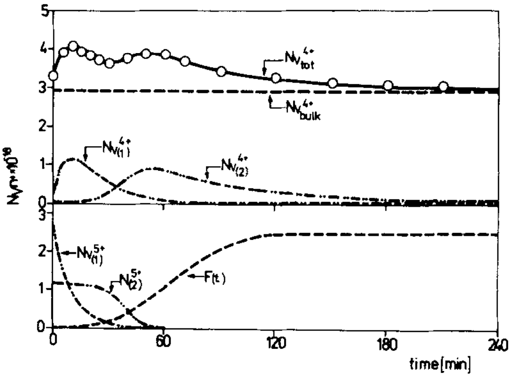

FIG. 6. The fitting of the theoretical kinetic curve $N_{V^{4+}_{tot}}(t)$ (solid line) to experimental data (circles) for propylene adsorption at 373 K on V_2O_5–MoO_3 containing 28.0 mol% MoO_3. The changes of $N_{V^{4+}_{(1)}}$, $N_{V^{4+}_{(2)}}$, $N_{V^{5+}_{(1)}}$, $N_{V^{5+}_{(2)}}$, and $F(t)$ with time of adsorption as well as the value of $N_{V^{4+}_{bulk}}$ are calculated from kinetic equations (see text).

i.e., the initial degree of reduction of the surface layers increased. The number of $V_{(1)}^{4+}$ ions engaged in the reduction process (related to the first maximum) at $t = 0$, denoted as $N_{V_{(1)}^{4+}}(0)$, increased with increase of the MoO_3 concentration. Similarly as in the course of oxygen adsorption (*1*), it reached a maximum value for the V_2O_5–MoO_3 catalyst with 21.0 mol% MoO_3. On the other hand, the number of $V_{(2)}^{4+}$ ions at $t = 0$ [$N_{V_{(2)}^{4+}}(0)$] taking part in the reactions related to the second maximum was practically the same for both catalysts with 3.4 and 21.0 mol% MoO_3, while for the catalyst with 28.0 mol% MoO_3 it was negligible. A similar effect was observed in the case of oxygen adsorption on this preparation (*1*). Two possible reasons for this effect should be considered: either the surface of the solid solution phase is blocked by Mo ions, or a good stabilization of $V_{(2)}^{4+}$ ions renders their reaction with propylene difficult.

On comparing the number of V^{4+} ions for a given catalyst involved at time $t = 0$ [$N_{V^{4+}}(0)$] in redox processes at 373 K it may be noticed that the number of both types of V^{4+} is 2–3 times higher in reduction than in oxidation processes (Table 2 of the present work and Table 3 in Ref. (*1*)). Thus the conclusion may be drawn that propylene is more active than oxygen in the reaction with partially reduced V_2O_5–MoO_3 catalysts.

Values of the rate constants $k_{A(1)}$ and $k_{B(1)}$ are close to each other, similarly as for the oxidation of vanadium ions stabilized in the vicinity of oxygen vacancies (*1*). On the other hand, the rate constants $k_{A(1)}$ for the catalysts studied were greater than that calculated for pure V_2O_5 (*6*), and they increased when the concentration of MoO_3 was raised. The rate constants $k_{B(1)}$ revealed a similar pattern of behavior. Assuming that the mechanism of these reactions in V_2O_5–MoO_3 was the same as that in reduced V_2O_5 (*6*), the increase in the values of the rate constants may be explained by an increasing heterogeneity of the catalysts.

Discussing the changes of the rate constants $k_{A(2)}$, the parameters a and t_s should be considered. The rate constants increased significantly with increase of the concentration of MoO_3, whereas the value of parameter a decreased and that of parameter t_s increased. The pattern of changes of parameters a and t_s with increasing MoO_3 concentration was quite opposite to that found in oxidation processes. The values of $k_{B(2)}$ were considerably lower than $k_{A(2)}$, probably due to stabilization of $V_{(2)}^{4+}$ ions.

The value of the parameter $N_{V_{bulk}^{4+}}$ corresponding to the number of V^{4+} ions which were not engaged in the reduction process, calculated from the kinetic equations, was consistent with that found on the plateau of the experimental curves $N_{V^{4+}}(t)$. The same relation was found for the oxidation process.

The number of metal ions participating in the reduction processes, found experimentally, was compared with the sum of $V_{(1)}^{5+}$ and $V_{(2)}^{5+}$ ions calculated from the kinetic equations after a certain period of propylene adsorption (Table 1). Subtracting the number of V^{4+} ions found from ESR measurements from the sum of V^{4+}, V^{3+}, and Mo^{4+} ions calculated from chemical analysis, the contents of V^{3+} and Mo^{4+} ions, not detectable by ESR, in both the initial preparations and those obtained after their contact with propylene for a certain period of time were computed (Table 1, column 4). Provided that only vanadium takes part in the reaction it was possible to calculate the number of V^{4+} and V^{3+} ions generated after a certain period of propylene adsorption (columns 5 and 6, respectively). Adding the numbers of V^{3+} and V^{4+} ions found in this way, the number of V^{5+} participating in the reduction processes was obtained. It proved to be higher than the sum of $V_{(1)}^{5+}$ and $V_{(2)}^{5+}$ calculated from the kinetic equations. Such a difference between experimental and calculated data may be explained, similarly as in the case of oxygen adsorption (*1*), by the presence of Mo^{6+} reducible in the course of propylene interaction. Such reduced molybdenum could be found not only in the surface layers of the V_2O_5–MoO_3 solid solution enriched with molybdenum but also in MoO_3 phase present in the catalysts (*1*).

The rate constants characterizing both oxidation and reduction of V^{4+} ions stabilized by oxygen vacancies are close to each other for a given catalyst. The rate of these processes is thus determined by the number of vanadium ions of various oxidation states. The observed increase in oxidation and reduction rate constants for $V^{4+}_{(1)}$ ions with increase of MoO_3 concentration can play an important role in the processes catalyzed by V_2O_5–MoO_3.

4. Physical Model of the Reduction Processes

In the course of pretreatment of vanadia–molybdena catalysts in vacuo, oxygen is removed from the lattice of the catalyst. This process is accompanied by diffusion of metal ions toward the bulk. The faster diffusion of vanadium in comparison with that of molybdenum leads to a relative enrichment of the surface layers with molybdenum. Interaction of V_2O_5–MoO_3 catalysts with propylene, consisting of further removal of lattice oxygen, results in further segregation. In order to assume electroneutrality of the lattice, an additional number of reduced metal ions appears in the catalysts.

We have assumed that at 373 K interaction of propylene with V_2O_5–MoO_3 is restricted to the near-to-surface layers. At the initial stage of propylene adsorption only oxygen localized on the surface is engaged in the reaction leading to the reduction of both vanadium and molybdenum present on the surface. The vanadium reduction is reflected by an appearance of the first maximum on the kinetic curves $N_{V^{4+}}(t)$. On the other hand, the reduction of molybdenum can be detected only by chemical analysis. The reduced vanadium ions situated on the surface are stabilized mainly by oxygen vacancies (*1*). In the course of further reduction the $V^{4+}_{(1)}$ and $V^{3+}_{(1)}$ ions migrate toward the bulk, resulting in a gradual exposure of the unreduced $V^{5+}_{(2)}$ ions in the solid solution phase. The reduction of these ions with propylene to $V^{4+}_{(2)}$ and then to $V^{3+}_{(2)}$, both stabilized mainly by Mo^{6+}, leads to the formation of the second maximum on the $N_{V^{4+}}(t)$ curves. The $V^{4+}_{(2)}$ signal intensity decreases very slowly after passing through the maximum, thus suggesting that the second step of reduction $V^{4+}_{(2)} \rightarrow V^{3+}_{(2)}$ is more difficult in V_2O_5–MoO_3 catalysts than in pure V_2O_5 (*6*), most probably due to a more effective stabilization of reduced vanadium.

In the catalyst with high MoO_3 content, i.e., of high degree of reduction, only a few $V^{5+}_{(1)}$ ions are present on the surface. In such a catalyst the surface becomes practically depleted of $V^{5+}_{(1)}$ ions just after the contact with propylene. Therefore, diffusion of reduced vanadium toward the bulk, followed by the exposure of $V^{5+}_{(2)}$ ions from deeper layers, should begin in such a catalyst earlier than in the less reduced one, namely that with a small amount of MoO_3 and a much higher number of $V^{5+}_{(1)}$ ions present at the surface. Indeed, in the catalyst containing 28.0 mol% MoO_3 the reaction $V^{5+}_{(2)} \rightarrow V^{4+}_{(2)}$, responsible for the appearance of the second maximum, is switched on practically at the beginning of propylene adsorption, whereas in the catalyst with the small amount of MoO_3 the induction period of reaction (2) is longer (Figs. 4–6).

In the kinetic model the delay in reduction of $V^{5+}_{(2)}$ ions in the phase of the solid solution of MoO_3 in V_2O_5 is described by modulation of Eqs. (6) and (7) by a sigmoid function. The rate of increase of this function is described by parameter a. Thus the parameter a controls the rate of the process leading to exposure of $V^{5+}_{(2)}$ ions for reduction. We have suggested that the rate of diffusion of reduced vanadium from the surface to the depper layers is a factor which determines this effect. The parameter a may therefore be interpreted, similarly as in the oxidation process (*1*), as a measure of the rate constant of diffusion of reduced vanadium in the V_2O_5–MoO_3 catalyst. The pattern of the changes of parameter a with increasing MoO_3 content is different for oxidizing and reducing atmosphere. This difference may be related to the fact that during reduction the vanadium ions diffuse from the surface (rich in molybdenum) toward the bulk (rich in vanadium) whereas during oxidation they diffuse in the opposite direction. Increasing the Mo concentration results in a decrease of the V concentration in the surface layers of the catalyst. Consequently, the rate of diffusion of vanadium toward the surface is enhanced during oxidation but the vanadium diffusion toward the bulk is delayed during reduction.

At higher temperatures the reduction process includes also the bulk of the catalysts. At 473 K the process occurring in the surface layers is related to the first maximum. The high intensity of the second maximum, strongly exceeding the value corresponding to the number of paramagnetic centers which can be produced on the surface, indicates that vanadium ions from the bulk are also involved. With increasing amount of MoO_3 the reduction of vanadium from the bulk becomes inhibited (Fig. 3). The results of the chemical analysis indicate, however, progressive reduction of the samples. This effect is probably connected with an extensive reduction of the surface layers strongly enriched with molybdenum. Due to the high concentration of Mo in these layers, the process of its reduction dominates, inhibiting reduction of vanadium from the bulk. The delay in vanadium reduction may also be due to the covering of the surface by the reduction products.

At 573 K only reduction of the bulk is observed. Evidently, reduction of the surface layers at this temperature is very rapid leading to the formation of $V^{3+}_{(I)}$ ions not visible by ESR.

CONCLUSIONS

Two different reduction processes occur in V_2O_5–MoO_3 catalysts upon interaction with propylene at 373 K. One of them involves the surface vanadium ions stabilized after reduction by oxygen vacancies. The other is connected with reduction of vanadium present in the near-to-surface layers of the V_2O_5–MoO_3 solid solutions which is stabilized after reduction by Mo^{6+}. The effective stabilization of V^{4+} ions in the V_2O_5–MoO_3 catalysts, postulated previously for the reaction of oxidation (*1*), has been confirmed also in the reduction process.

The engagement in the reduction process of the metal ions from the near-to-surface layers or from the bulk is controlled both by temperature and by the content of MoO_3. The role of MoO_3 consists in determination of the reduction degree of the catalysts and in influencing, by the segregation processes, the rate of diffusion of reduced vanadium from the surface toward the bulk.

The proposed reduction model is consistent with the previously described model of oxidation reactions occurring in the V_2O_5–MoO_3 system (*1*).

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