

## Regeneration of Catalysts Based on Aqueous Solutions of Mo-V-Phosphoric Acids under Increased O<sub>2</sub> Pressure

E. G. ZHIZHINA, M. V. SIMONOVA, V. F. ODYAKOV and K. I. MATVEEV

*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)*

*E-mail: zhizh@catalysis.nsk.su*

(Received November 26, 2003)

### Abstract

Oxidation of the 0.2 M solutions of  $H_{7+m}PV_m^{IV}V_{4-m}^V Mo_8O_{40}$  ( $H_m$ HPA-4) by oxygen at temperatures from 373 to 433 K under O<sub>2</sub> pressure up to 8 ata (810 kPa) is investigated. The maximal reaction rate is observed at 433 K. At a higher temperature, partially oxidized 0.2 M solutions of  $H_m$ HPA-4 are thermally unstable. With an increase in the extent of oxidation of  $H_m$ HPA-4 solutions, the apparent activation energy increases.

### INTRODUCTION

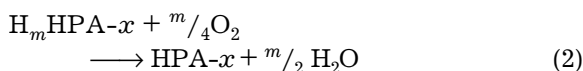
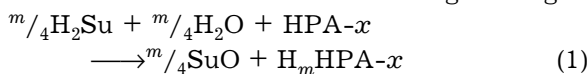
Vanadium-containing heteropolyacids of Keggin structure having the composition  $H_{3+x}PV_x^V Mo_{12-x}O_{40}$  (HPA- $x$ ,  $2 \leq x \leq 6$ ) attract much attention due to their unique physico-chemical properties. These compounds are strong acids and strong oxidizers; their reduced forms are able to get oxidized with molecular oxygen [1], so concentrated aqueous solutions of HPA- $x$  can be used as reversible oxidizers, that is, catalysts of the oxidation of different substrates with oxygen. The ability to be regenerated under the action of oxygen is a distinguishing feature of HPA- $x$  in comparison with such irreversible oxidizers as the compounds of chromium (VI), cerium (IV), manganese (VII) [2]; their reduced forms either require thorough processing [for example, cerium (III)] or are hazardous industrial wastes (chromium (III)). In the processes participated by HPA- $x$ , the oxidizing agent is cheap and ecologically friendly O<sub>2</sub>. The structure of HPA- $x$  is conserved in these processes; in the reduced state this catalyst has a composition

$H_{3+x+m}PV_m^{IV}V_{x-m}^V Mo_{12-x}O_{40}$ , or  $H_m$ HPA- $x$  ( $m$  is the number of electrons accepted by HPA- $x$  molecule)<sup>a</sup>.

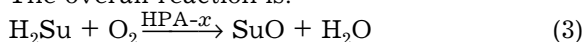
A number of low-waste catalytic processes was developed within the recent twenty years on the basis of the aqueous HPA- $x$  solutions [1]. Among the home developments, «Vikasib» technology is to be mentioned (the synthesis of vitamin K<sub>3</sub>); its key stage is catalytic oxidation of 2-methyl-1-naphthol into 2-methyl-1,4-naphthoquinone in the presence of HPA- $x$  [4]. Selective catalytic oxidation of 2,3,6-trimethylphenol into 2,3,5-trimethyl-1,4-benzoquinone (>98 %) was developed as a stage of the multi-stage synthesis of vitamin E [4, 5]. The introduction of new catalytic oxidation processes participated by HPA- $x$  solutions will allow one to decrease the number of stages, diminish energy consumption and provide ecological safety of these processes.

<sup>a</sup>The form of  $H_m$ HPA- $x$  reduced by  $m$  electrons contains  $x$  vanadium atoms, including  $m$  atoms of vanadium (IV), that is, 0 J m J x.

Usually the oxidation of substrates  $\text{H}_2\text{Su}$  in the presence of  $\text{HPA-}x$  solutions is carried out in different reactors in two technological stages:

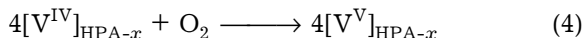


The overall reaction is:



Separate performance of reactions (1) and (2) provides high selectivity of reaction (1). The solutions of  $\text{H}_m\text{HPA-}x$  are mixtures of anions  $[\text{H}_{x+m-1}\text{PV}_m^{\text{IV}}\text{V}_{x-m}^{\text{V}}\text{Mo}_{12-x}\text{O}_{40}]^{4-}$  (HPA- $x$  with different integer-valued  $m$ , including  $m = 0$ ), as well as  $\text{VO}^{2+}$  and  $\text{VO}_2^+$  cations [6]; therefore, the average degree of reduction of these solutions is  $m^* = [\text{V}^{\text{IV}}]/[\text{H}_m\text{HPA-}x]$ , where  $[\text{V}^{\text{IV}}]$  is total concentration of  $\text{V}^{\text{IV}}$ , and  $[\text{H}_m\text{HPA-}x]$  is total concentration of HP anions which is equal to the initial concentration of  $\text{HPA-}x$  before reaction (1).

During reaction (2), vanadium (IV) in HP anions gets oxidized to form vanadium (V), so  $m^*$  decreases:



An important condition for the use of  $\text{HPA-}x$  solutions as the catalysts of oxidation of different substrates is maximally deep oxidation of  $\text{H}_m\text{HPA-}x$  according to reaction (2). However, with a decrease in  $m^*$  the rate of this reaction decreases rapidly [7], which causes incomplete oxidation of the solutions of  $\text{H}_m\text{HPA-}x$ . For example, the 0.2 M solutions of  $\text{H}_m\text{HPA-}4$  (which are most active among  $\text{H}_m\text{HPA-}x$ ) under  $\text{O}_2$  at atmospheric pressure and at a temperature of 363 K are oxidized by oxygen only to the final value of  $m_{\text{fin}}^* \sim 1.06$  [7]. In the case of incomplete oxidation of  $\text{H}_m\text{HPA-}x$ , the productivity of catalysts in the overall reaction (3) decreases; this brings complications into the industrial introduction of catalytic processes according to scheme (1) + (2).

In the present work we make an attempt to increase the depth and rate of oxidation of  $\text{H}_m\text{HPA-}x$  solutions due to an increase in reaction temperature and  $\text{O}_2$  pressure. Investigation of the oxidation of 0.2 M solutions of  $\text{H}_m\text{HPA-}4$  was carried out within temperature range 373–433 K and partial pressure of  $\text{O}_2$  ( $p_{\text{O}_2}$ ) from 0.1 to 8 ata (10.1–810 kPa).

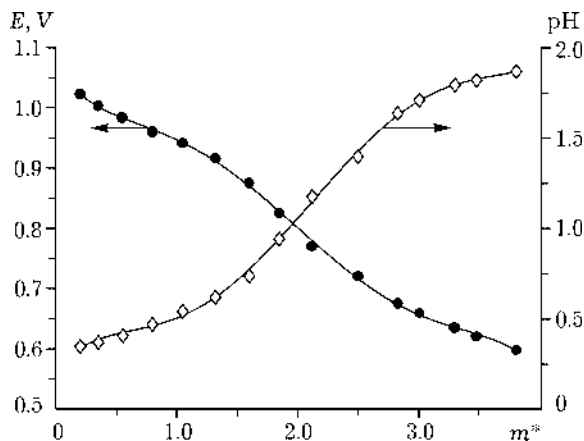


Fig. 1. Dependences of redox potential  $E$  and pH of 0.2 M  $\text{H}_m\text{HPA-}4$  solutions on the degree of reduction  $m^*$ .

## EXPERIMENTAL

Aqueous 0.2 M solutions of  $\text{HPA-}4$  were prepared according to the procedure described in [8] using  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$  and  $\text{H}_3\text{PO}_4$ . Before experiments, all the solutions were reduced with the aqueous solution 9 M  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  to  $\text{H}_m\text{HPA-}4$  [9] (in the reduced solution, the initial  $m_r^* = 3.83$  corresponded to the redox potential  $E_r = 0.595$  V). The empirical dependence  $E = f(m^*)$  (Fig. 1) served as the calibration curve allowing us to determine  $m^*$  on the basis of  $E$  value without using the solution of  $\text{H}_m\text{HPA-}4$  [10].

Reaction (2) was investigated in a thermostated autoclave made of stainless steel 150 ml in volume, equipped with a backflow condenser. A glass containing 20 ml of  $\text{H}_m\text{HPA-}4$  solution and a magnetic rod was placed in the autoclave. The autoclave was closed with a cap and placed on a magnetic mixer.

The  $\text{H}_m\text{HPA-}4$  solution was thermostated for 10 min at the necessary temperature without supplying  $\text{O}_2$  and without mixing. Then  $\text{O}_2$  was supplied at a given pressure ( $p_{\text{total}} = p_{\text{O}_2} + p_{\text{H}_2\text{O}}$ ) into the autoclave through a metal capillary to the surface of solution; pressure was measured with a reference manometer with an accuracy of  $\pm 0.05$  ata. Before the experiment, the autoclave was blown with a weak flow of  $\text{O}_2$  for 1 min. Then the magnetic mixer was switched on (700 rpm)<sup>b</sup> along with a timer (stop-watch).

<sup>b</sup>Rotation rate of the magnetic rod of the stirrer was kept below 700 rpm to avoid possible breaks in stirring and spraying of solution.

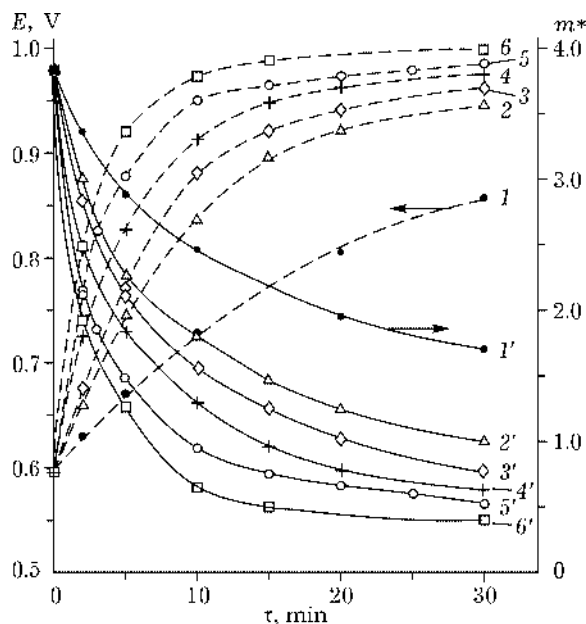


Fig. 2. Dependences of the final  $E_{\text{fin}}$  and  $m^*_{\text{fin}}$  values on the time of oxidation of 0.2 M  $H_m\text{HPA-4}$  solutions by oxygen at different temperatures, K: 373 (1, 1'), 393 (2, 2'), 403 (3, 3'), 413 (4, 4'), 423 (5, 5'), 433 (6, 6').  $p_{\text{O}_2} = 4$  ata,  $E_r = 0.595$  V,  $m^*_\tau = 3.83$ .

Weak  $\text{O}_2$  flow provided the absence of stagnant zones in the autoclave. Water vapour carried away with the  $\text{O}_2$  flow were condensed in the backflow condenser; water trickled down into the  $H_m\text{HPA-4}$  solution.

The reaction was carried out for the necessary time interval (2 to 30 min), then the mixer was switched off, autoclave heating was ceased,  $\text{O}_2$  pressure was thrown off as rapidly as possible through the backflow condenser; the autoclave was unsealed. The solution under investigation was cooled to room temperature; water was added until the solution volume became 20 ml. (Within the time of experiment the solution got evaporated not more than by 0.3–0.4 ml.)

After completion of reaction (2), the value of  $m^*_{\text{fin}}$  was determined, as a rule, on the basis of the final redox potential value  $E_{\text{fin}}$  of the oxidized  $H_m\text{HPA-4}$  solution [10] which was measured at room temperature with the help of the digital I-130 ion meter with the EPV platinum electrode and saturated silver chloride reference ESL-1M3 electrode. A constant value of  $E_{\text{fin}}$  was established within 2–3 min with an accuracy of  $\pm 0.001$  V.

In some experiments, the concentration of residual  $\text{V}^{\text{IV}}$  and  $m^*_{\text{fin}}$  were measured more pre-

cisely by means of potentiometric titration with  $\text{KMnO}_4$  solution [11]. The error of  $m^*_{\text{fin}}$  determination from the  $E = f(m^*)$  curve did not exceed  $\pm 3\%$  in comparison with  $m^*_{\text{fin}}$  determination by means of titration with  $\text{KMnO}_4$ .

Each experiment on  $H_m\text{HPA-4}$  oxidation was reproduced 3–5 times in order to determine average  $E_{\text{fin}}$  and  $m^*_{\text{fin}}$  values. The  $m^* = f(\tau)$  curves were plotted for different temperatures on the basis of the entire set of experiments carried out for  $p_{\text{O}_2} = \text{const} = 4.0$  ata (405 kPa) and varied  $\tau$ . Using the  $m^*_\tau$  and  $m^*_{\tau+\Delta\tau}$  values determined with the help of these plots, we calculated the mean rate of  $\text{O}_2$  absorption by the  $H_m\text{HPA-4}$  solution for the region of the curve from  $m^*_\tau$  and  $m^*_{\tau+\Delta\tau}$ :

$$W_2 = (0.2/4)\Delta m^* \Delta \tau \quad (5)$$

Here  $W_2$  is the rate of reaction (4), mol  $\text{O}_2$ /(l min),  $\Delta m^*$  is the change in  $m^*$  during the time interval  $\Delta\tau$  equal to  $m^*_\tau - m^*_{\tau+\Delta\tau}$ ;  $\Delta\tau$  is a change in  $\tau$ , min; 0.2 is the concentration of  $H_m\text{HPA-4}$ , mol/l; 4 is the stoichiometric coefficient in reaction (4).

Reaction rates  $W_2$  for  $m^*$  equal to 1.45 and 0.80 were determined from the tangent (slope ratio)  $\Delta m^*/\Delta\tau$  of the curves  $m^* = f(\tau)$  (see Fig. 2). The obtained values were multiplied by  $0.2/4 = 0.05$  according to equation (5).

If precipitation occurred during investigation of the solution of  $H_m\text{HPA-4}$ , the precipitates were filtered and washed with water. Their vanadium (IV) and (V) content was determined using the procedure described in [12].

## RESULTS AND DISCUSSION

During the reduction-oxidation processes in  $\text{HPA-}x$ , transformations are underwent by vanadium [ $\text{V}^{\text{V}} \leftrightarrow \text{V}^{\text{IV}}$ ]. It should be noted that vanadium (IV) in the form of cation  $\text{VO}^{2+}$  is almost entirely non-oxidized by oxygen in aqueous solutions [13], but it is rather easily oxidized when incorporated in HP anions [7]. The acidity of the  $H_m\text{HPA-4}$  solution increases during its oxidation (see Fig. 1).

In the beginning of reaction (2), in the case of high  $m^*$  values ( $m^* > 3$ ), the oxidation rate is very high, but it drops down rapidly as  $m^*$  decreases<sup>c</sup>.

<sup>c</sup>Such a drop of the reaction rate was observed previously at atmospheric pressure of  $\text{O}_2$  [7]; a decrease in  $m^*$  was accompanied by the change in the limiting stage of reaction.

TABLE 1

Effect of temperature of oxidation of the 0.2 M  $H_m$ HPA-4 solution by oxygen on the final degree of reduction  $m_{fin}^*$  ( $p_{O_2}^* = 4$  ata (405 kPa),  $m_r = 3.83$ ,  $\tau = 30$  min)

$T$ , K	$m_{fin}^*$	$T$ , K	$m_{fin}^*$
373	1.70	413	0.63
393	1.00	423	0.52
403	0.76	433	0.40

With an increase in reaction time  $\tau$ , the redox potential  $E$  increases and  $m^*$  decreases (see Fig. 2), which is the evidence of more complete oxidation of the  $H_m$ HPA-4 solution. Maximal growth of  $E$  is observed at 433 K. At this temperature, the final  $m_{fin}^*$  decreases to 0.40 (Table 1).

Further increase in temperature would likely allow deeper oxidation of  $H_m$ HPA-4 solutions. However, we discovered that at  $T > 433$  K partially oxidized 0.2 M  $H_m$ HPA-4 solutions start to form precipitates which are similar to hydrated mixed-valent oxides of vanadium (V) and vanadium (IV) described precisely [14, 15]. It is essential that such precipitates are not formed till 463 K in the initial strongly reduced solutions of  $H_m$ HPA-4 ( $m^* > 3$  in the absence of  $O_2$ ).

Precipitates formed at  $T > 433$  K did not dissolve in 0.2 M solution of  $H_m$ HPA-4; therefore, it gets depleted in vanadium. So, the

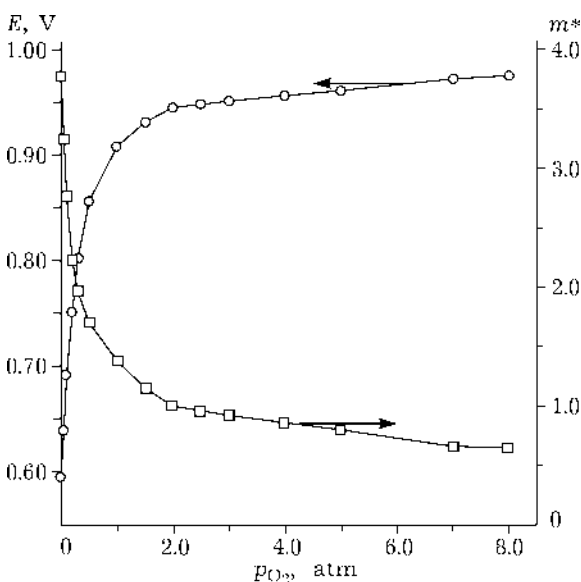


Fig. 3. Dependence of  $E$  and  $m^*$  on  $p_{O_2}$  for oxidation of 0.2 M  $H_m$ HPA-4 solutions.  $T = 423$  K,  $t = 10$  min,  $E_r = 0.595$  V,  $m_r^* = 3.83$ .

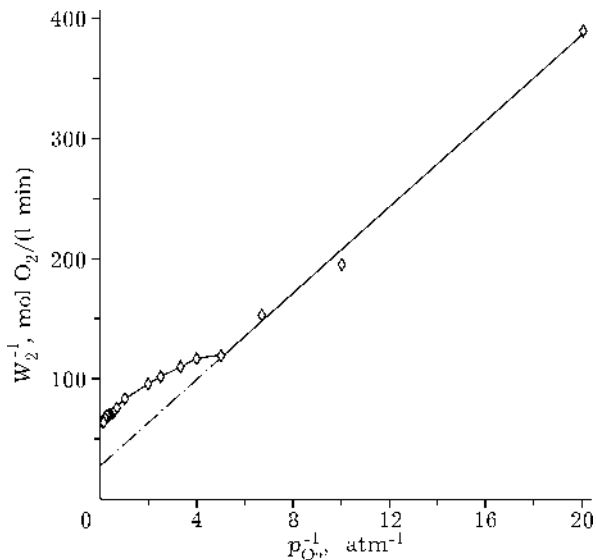


Fig. 4. Dependence of the mean oxidation rate  $W_2^{-1}$  on reciprocal partial pressure of  $O_2$ .  $T = 423$  K,  $t = 10$  min,  $E_r = 0.595$  V,  $m_r^* = 3.83$ .

0.2 M  $H_m$ HPA-4 solutions oxidized at  $T > 433$  K are thermally unstable; the region of their application as catalysts is limited by the temperature point of 433 K.

The dependence of completeness of oxidation of  $H_m$ HPA-4 solutions on  $p_{O_2}$  is shown in Fig. 3. One can see that the completeness, and therefore mean oxidation rate, increases with an increase in  $p_{O_2}$ . The  $W = f(p_{O_2})$  dependence for  $p_{O_2} \leq 0.2$  ata (20.3 kPa) turned out to be linear (Fig. 4). Its deviation from the linear form for higher  $p_{O_2}$  is explained by the diffusion braking of reaction (2) at its high rates. Since the mixing rate is limited in our experiments, the fast reaction proceeds in the diffusion region at the initial moment of time.

A similar linear dependence  $W_2^{-1} = k_{obs}[O_2]^{-1} + K_{obs}W_{2max}^{-1}$  [16, 17] was obtained previously in the kinetic studies of model systems with diluted solutions of  $H_m$ HPA-4 in buffer solutions under atmospheric pressure of  $O_2$ .

Temperature dependencies of the rate of reaction (2) are shown in Fig. 5. At the initial region of reaction for  $3.83 > m^* > 2.5$  the apparent activation energy is  $E_a \approx 32$  kJ/mol. With a decrease in  $m^*$  to 1.45 and 0.80,  $E_a$  increases to 51 and 88 kJ/mol, respectively<sup>d</sup>.

<sup>d</sup>According to the preliminary data obtained by us, for  $p_{O_2} + p_{H_2O} = 1$  ata even stronger increase in  $E_a$  to  $\sim 200$  kJ/mol is observed.

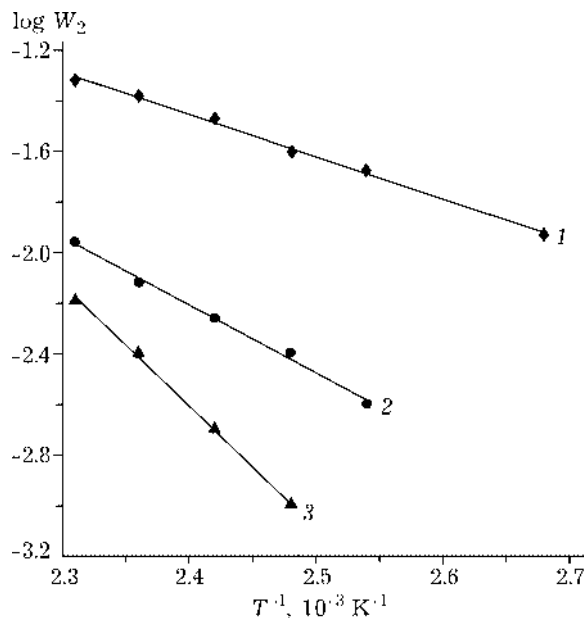
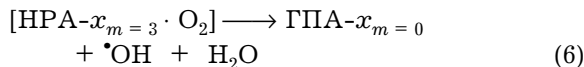
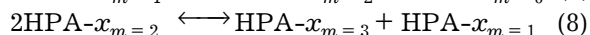
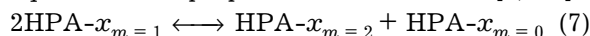


Fig. 5. Dependence of  $\log W_2$  on reciprocal absolute temperature for different degrees of reduction of 0.2 M  $H_m$ HPA-4 solution at  $p_{O_2} = 4$  ata. The  $m^*$  values: 3.8–2.5 (1), 1.45 (2), 0.80 (3).

It is very difficult to reveal the mechanism of reaction (2) because of a large number of equilibria occurring in HPA- $x$  and  $H_m$ HPA- $x$  solutions [6]. These equilibria are participated by many anions of HPA- $x$  with different  $m$  and  $x$  [7]; however, only the HPA- $x$  ions in which  $m \geq 3$  are active in the reaction with  $O_2$ . They form intermediate active complexes with  $O_2$ ; these complexes of  $[HPA-x_{m=3} O_2]$  type decompose according to reaction [16–18]:



For small  $m^*$ , these HP anions are formed in the equilibrium disproportionation reactions [7, 18]:

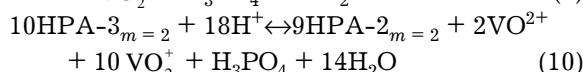
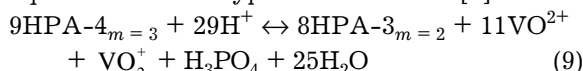


We showed previously that the heat of reaction (2) (that is,  $-\Delta H_{2r}$ ) is a variable value decreasing with a decrease in  $m^*$  [9]. We suppose that  $E_a$  is variable since in the case of decrease in  $m^*$  the heat of the equilibrium stages (7) and (8) is added to the true activation energy of stage (6).

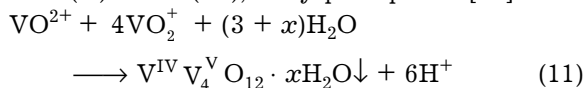
As we have already mentioned, a decrease in  $m^*$  is accompanied by a decrease in pH of  $H_m$ HPA-4 solution (see Fig. 1). Since an increase in temperature of reaction (2) causes an increase in the reaction rate and a decrease in  $m_{fin}^*$  (see

Table 1), at temperatures above 433 K, the rapidly achieved pH values of  $H_m$ HPA-4 solutions are lower than those for  $T < 433$  K<sup>e</sup>.

In this process, due to the equilibrium with  $H^+$  ions, the HPA- $x_{m=3}$  anions that are active towards oxygen form inactive anions of HPA- $x_{m \leq 2}$  and cations ( $VO^{2+}$  and  $VO_2^+$ ) according to equations of the type mentioned in [6]:



In  $H_m$ HPA-4 solution heated to  $T > 433$  K, the concentrations of  $VO^{2+}$  and  $VO_2^+$  cations are so high that these ions start to hydrolyze with the formation of mixed hydrated oxides of V(V) and V(IV); they precipitate [15]:



In deeply reduced  $H_m$ HPA-4 solutions ( $m^* > 3$ ), the concentration of  $VO_2^+$  ions is small;  $VO^{2+}$  cations are hydrolyzed to form  $VO(OH)_2$  at rather high pH (~4–5) [19]. Even in the case of deep reduction of HPA-4 solutions, such a value of pH is never achieved (see Fig. 1), that is why the precipitates containing vanadium (IV) are not formed.

## CONCLUSIONS

The deepness and rate of oxidation of the reduced HPA-4 solutions ( $H_m$ HPA-4) by oxygen increase with temperature rise from 373 to 433 K and oxygen pressure increase from 0.1 to 8 ata.

Above 433 K, partially oxidized 0.2 M  $H_m$ HPA-4 solutions become thermally unstable and release precipitates of the hydroxides of V<sup>V</sup> and V<sup>IV</sup> of mixed valence. As a consequence, the region of application of the catalysts based on HPA-4 solutions is limited by the temperature point of 433 K.

The apparent activation energy of the oxidation of  $H_m$ HPA-4 solution by oxygen is a

<sup>e</sup>For example, in the case of  $m^* < 1.5$  at room temperature, pH of 0.2 M  $H_m$ HPA-4 solution becomes lower than 0.8. According to our data, with an increase in temperature, pH of the solutions of  $H_m$ HPA-4 with given  $m^*$  values decreases.

variable value; it increases while the depth of oxidation of  $H_m$ HPA-4 increases.

The possibility of deep oxidation of the reduced solutions of HPA- $x$  at elevated temperature under  $O_2$  pressure opens the outlooks of developing ecologically safe technologies of the catalytic oxidation of various substrates by oxygen in the presence of HPA- $x$  solutions.

#### REFERENCES

- 1 I. V. Kozhevnikov, *Catalysis for Fine Chemical Synthesis*, vol. 2: *Catalysis by Polyoxometalates*, J. Wiley & Sons, Chichester, 2002, pp. 117–136.
- 2 M. Hudlicky, *Oxidation in Organic Chemistry*: ACS Monograph 186, ACS, Washington, 1990, pp. 94–96.
- 3 M. S. Pop, *Geteropoli- i izopolimetallaty*, Nauka, Novosibirsk, 1990, pp. 137–138.
- 4 K. I. Matveev, E. G. Zhizhina, V. F. Odyakov, *Khim. Prom-st.*, 3 (1996) 173.
- 5 Pat. 2165406 RF, 2001.
- 6 V. F. Odyakov, E. G. Zhizhina, K. I. Matveev, *Zh. Neorg. Khim.*, 45 (2000) 1379.
- 7 E. G. Zhizhina, V. F. Odyakov, M. V. Simonova, K. I. Matveev, *React. Kin. Cat. Lett.*, 78 (2003) 373.
- 8 V. F. Odyakov, E. G. Zhizhina, R. I. Maksimovskaya, K. I. Matveev, *Kinet. Kataliz.*, 36 (1995) 795.
- 9 E. G. Zhizhina, V. F. Odyakov, K. I. Matveev, *Eur. J. Inorg. Chem.*, 6 (1999) 1009.
- 10 E. G. Zhizhina, V. F. Odyakov, K. I. Matveev, *Zh. Prikl. Khim.*, 73 (2000) 777.
- 11 L. S. A. Dikshitulu, G. Gopala Rao, *Fresenius' Z. anal. Chemie*, 189 (1962) 421.
- 12 T. I. Bocharova, V. V. Malakhov, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 6 (78) 104.
- 13 H. T. S. Britton, *J. Chem. Soc.*, 11 (1934) 1842.
- 14 A. A. Ivakin, I. G. Chufarova, N. I. Petunina *et al.*, *Zh. Neorg. Khim.*, 22 (1977) 214.
- 15 J. Lemerle, L. Nejem and J. Lefebvre, *J. Inorg. Nucl. Chem.*, 43 (1981) 2683.
- 16 V. M. Berdnikov, L. I. Kuznetsova, K. I. Matveev *et al.*, *Koordinats. Khim.*, 5 (1979) 78.
- 17 L. I. Kuznetsova, V. M. Berdnikov, K. I. Matveev, *React. Kin. Cat. Lett.*, 17 (1981) 401.
- 18 I. V. Kozhevnikov, Yu. V. Burov, K. I. Matveev, *Izv. AN SSSR. Ser. Khim.*, 11 (1981) 2428.
- 19 O. Glemser, E. Schwarzmann, *Z. anorg. allgem. Chemie*, 278 (1955) 249.