Homogeneous Redox Catalysts Based on Heteropoly Acid Solutions: IV. Tests of Methyl Ethyl Ketone Synthesis Catalysts in the Presence of Equipment Corrosion Products (Metal Cations)

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Abstract—The effect of equipment corrosion products (transition metal cations) on the physicochemical and catalytic properties of a homogeneous Pd(II)+HPA-x (Mo−V−P heteropoly acid containing x vanadium atoms) catalyst developed for the two-stage oxidation of n-butene to methyl ethyl ketone (MEK) with oxygen has been studied. The thermal stability of a solution of a catalyst based on HPA-x in the presence of transition metal cations has been determined. The composition of the two-component catalyst recommended for pilot testing of the MEK process has been optimized.

INTRODUCTION

Solutions of molybdovanadophosphoric heteropoly acids (HPA-x, where x is the number of vanadium atoms in the HPA) have been used in oxidation catalysis for about 50 years. It has been found that these solutions exhibit a number of unique properties, the main of which is reversible oxidizability, i.e., the ability of reduced HPA-x solutions to be oxidized by molecular oxygen. This feature has made it possible to close two-stage catalytic cycles of oxidation of substrates of different classes with oxygen in the presence of HPA-x solutions [1]. Over the past years, considerable experience in using HPA-x solutions has been accumulated, and a large number of catalytic reactions in their presence have been studied [2−11]. Initially, only low-vanadium Keggin HPA-x solutions ($H_{3+x}PMo_{12−x}V_xO_{40}$, $x \leq 4$) were used; however, later, methods for synthesizing modified (non-Keggin) high-vanadium HPA-x solutions exhibiting a significantly higher thermal stability and productivity were developed [12].

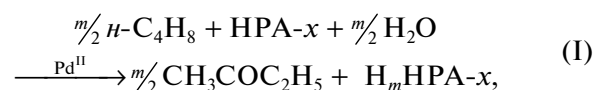Modified HPA-x solutions provided the rapid occurrence of the stage of regeneration of catalysts based on them with oxygen (air) at high temperatures (160−190°C) and thereby opened up the prospect of the industrial implementation of oxidation processes involving HPA-x solutions. It should be noted that, in the case of Keggin solutions, it was the regeneration of HPA-x with oxygen that was the key stage, because it caused the most significant problems in the implementation of catalytic processes owing to the low rate of regeneration and precipitation at $T > 135°C$ [13].

It was found that modified HPA-x solutions can be used as highly efficient catalysts not only for oxidation reactions. Since these solutions have a high Brønsted acidity, they are effectively used as bifunctional (acid and oxidation) catalysts [10]. Owing to high activities and selectivities in the target reactions and the effective solution of the problem of regenerating catalysts based on modified HPA-x solutions, a number of the developed processes were subjected to pilot testing. However, in this case, some technological tasks arose, for which data on the physicochemical properties of HPA-x solutions (density, viscosity, pH, redox potential E [14], electrical conductivity [15], corrosion properties [16, 17]) and changes in these properties during redox reactions are of particular significance. In this context, data on the effect of equipment corrosion products (transition metal cations), in particular, in pilot plants, on the state of a homogeneous HPA-x-based catalyst designed for long-term operation are also of considerable importance. Below, using the example of one of the developed processes based on an HPA-x solution, it will be shown how some important

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Abbreviations and notation: HPA, heteropoly acid; MEK, methyl ethyl ketone; Pc, cobalt dichlorodisulfophthalocyanine disodium salt; E, redox potential; GLC, gas−liquid chromatography; NHE, normal hydrogen electrode; m, degree of reduction of the HPA-x solution; Δm, change in the degree of reduction of the HPA-x solution during reaction; τ_{but}, butylene reaction time; τ_{oxyg}, catalyst regeneration time; W_{but}, butylene absorption rate.

technological problems arising during the preparation of pilot tests were solved.

Thus, this study is a continuation of a series of studies [18, 19] of a homogeneous Pd(II)+HPA-x catalyst developed at Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences for the pilot industrial implementation of a two-stage process for the oxidation of n-butylene to methyl ethyl ketone (MEK) with oxygen [20, 21] in accordance with reactions (I) + (II). The occurrence of these reactions in different reactors provided a 98% selectivity and explosion safety of the MEK process:

$$\frac{m}{2}\,\textit{н}\text{-C}_4\text{H}_8 + \text{HPA-}x + \frac{m}{2}\,\text{H}_2\text{O}$$
$$\xrightarrow{\text{Pd}^{II}} \frac{m}{2}\,\text{CH}_3\text{COC}_2\text{H}_5 + \text{H}_m\text{HPA-}x, \quad \text{(I)}$$

$$\text{H}_m\text{HPA-}x + \frac{m}{4}\,\text{O}_2 \rightarrow \text{HPA-}x + \frac{m}{2}\,\text{H}_2\text{O}. \quad \text{(II)}$$

Here, $\text{H}_m\text{HPA-}x$ $(\text{H}_{3+x+m}\text{PV}_m^{IV}\text{V}_{x-m}^{V}\text{Mo}_{12-x}\text{O}_{40})$ is the reduced form of HPA-x and m is the degree of reduction of the HPA-x solution, which is calculated by the formula: $m = [\text{V(IV)}]_\Sigma / [\text{HPA-}x]$. The m value can vary from 0 to x $(0 \le m \le x)$.

At the first stage of this process (butylene reaction), n-butylene is oxidized at 50−60°C with the Pd(II) complex to MEK, and the resulting Pd(0) is immediately oxidized to Pd(II) with Mo−V−P HPA. Thus, during reaction (I), a gradual reduction of the HPA-x solution, along with the formation of the product, occurs; the degree of reduction of the solution depends on the V(V) concentration in it. Next, after MEK stripping, at stage (II), the catalyst solution is regenerated with oxygen (air) at temperatures of 160−190°C and $P_{\text{O}_2} = 0.4$ MPa (oxygen reaction) [18]. After regeneration, the oxidized solution of the Pd(II) + HPA-x catalyst is ready again for use as a reversible oxidizing agent in the next cycle of the catalytic oxidation of n-butylene with oxygen. Hence, in an unsteady two-stage (I) + (II) catalytic MEK process, HPA-x (reversible oxidizing agent) is actually a component of the Pd(II) + HPA-x catalyst.

The new MEK process has passed pilot tests; the main results of the tests are described in [18]. It was found that an aqueous solution of a catalyst based on HPA-x is highly corrosive toward most steels. It was shown [16] that titanium is the only material that exhibits a high corrosion resistance with respect to this catalyst. Therefore, in developing the MEK process technology, it was initially planned to implement the process using the equipment made entirely of titanium. However, during the design work, it became clear that it was necessary to use special steels instead of titanium for shut-off and control valves and for individual units of the pilot industrial plant for MEK synthesis.

The use of special steels appropriate for operation in contact with a Pd(II) + HPA-x catalyst significantly increased the scale and complexity of problems to be solved to implement the MEK process. The list of these problems was supplemented, in addition to the determination of the resistance of steels, with the intractable problem of overcoming the negative effect of corrosion products on the performance, properties, and service life of the homogeneous catalyst. It was necessary to conduct a fairly large amount of studies to solve these problems.

According to detailed studies of corrosion of five types of special steels described in [16], two least corrosive samples were selected. It was found that steel 06KhN28MDT (EI-943) is the best substitute for titanium; steel Kh17N13M2T and similar steel Kh17N13M3T exhibit a lower corrosion resistance.

Based on the known composition of the corrosion products of this group of steels (M = $\text{Fe}^{2+(3+)}$, Cr^{3+}, Ni^{2+}) and the experimentally determined maximum allowable (MA) content of M cations in the catalyst solution (<0.1 M), we artificially introduced these cations into a homogeneous catalyst based on an HPA-7 solution with a gross composition of $\text{H}_{10}\text{P}_3\text{Mo}_{18}\text{V}_7\text{O}_{84}$ for a detailed study. Note that it was an HPA-7 solution that was used as the base solution (most stable and efficient) for synthesizing a two-component Pd(II) + HPA-x catalyst used to optimize the MEK process. Therefore, it was an HPA-7 solution that was used to conduct a number of basic studies, in particular, studies of physicochemical and corrosion properties [14, 17].

The prepared Pd(II) + HPA-7 samples with various M impurities (see below) were tested in several cycles of the MEK process (butylene + oxygen reactions). In addition, the samples were tested for thermal stability. In this manuscript, data of a comprehensive study of the effect of transition metal cations on the catalyst activity and stability in the two stages of the MEK process are described. The conclusions drawn according to these data provided an optimization of the homogeneous MEK synthesis catalyst prior to pilot testing [18, 19].

EXPERIMENTAL

Synthesis Procedure for an HPA-7 Solution

The 0.25 M aqueous solution of HPA-7 with a gross composition of $\text{H}_{10}\text{P}_3\text{Mo}_{18}\text{V}_7\text{O}_{84}$ that was used in this study was synthesized from V_2O_5, H_3PO_4, MoO_3, and H_2O_2 as described in [12]. At the beginning of the synthesis, V_2O_5 was dissolved in a cooled (4−5°C) and dilute H_2O_2 solution. The resulting peroxyvanadium compounds underwent spontaneous decomposition to give a dilute $\text{H}_6\text{V}_{10}\text{O}_{28}$ solution, which was immediately stabilized by adding excess H_3PO_4. The resulting solution was intermittently added to a gradually evaporated suspension ($\text{MoO}_3 + \text{H}_3\text{PO}_4$). Eventually, a homogeneous 0.25 M HPA-7 solution was prepared; the solution composition was controlled by ^{31}P and ^{51}V nuclear magnetic resonance spectroscopy [22].

Synthesis Procedure for Catalysts Containing Corrosion Products of Special Steels

A number of Pd(II) + HPA-7 catalyst samples with metal cations—corrosion products of special steels (Me = $Fe^{2+(3+)}$, Cr^{3+}, Ni^{2+})—were prepared for testing in the butylene reaction. To this end, the parent 0.25 M HPA-7 solution ($H_{10}P_3Mo_{18}V_7O_{84}$) was initially admixed with a calculated amount of 0.1 M $PdSO_4$ to obtain [Pd] = 6×10^{-3} M and then with a phthalocyanine (Pc) ligand, where Pc is the cobalt dichlorodisulfophthalocyanine disodium salt (manufactured by OOO Khimpolymer, Tambov), which was taken in a concentration of 9×10^{-3} M and used as a palladium stabilizer [20, 21].[1]

Eventually, a sufficient volume of a standard catalyst solution was prepared; it was subjected to partial neutralization to prepare solutions of catalysts based on HPA-7 acid salts. Catalysts based on salts of the following compositions were synthesized: (i) $Ni_{0.2}H_{9.6}P_3Mo_{18}V_7O_{84}$ ($Ni_{0.2}HPA$-7), (ii) $Fe_{0.2}H_{9.4}P_3Mo_{18}V_7O_{84}$ ($Fe_{0.2}HPA$-7), (iii) $Fe_{0.1}H_{9.7}P_3Mo_{18}V_7O_{84}$ ($Fe_{0.1}HPA$-7), and (iv) $Cr_{0.2}H_{9.4}P_3Mo_{18}V_7O_{84}$ ($Cr_{0.2}HPA$-7).

Thus, the $Ni_{0.2}HPA$-7 catalyst was synthesized by introducing a weighed portion of base nickel carbonate into a standard 0.25 M catalyst solution based on HPA-7 (with Pd and Pc) and subsequently boiling the solution for 5 min. After cooling, the solution volume (20 mL) was controlled and the redox potential E of the solution was measured.

The $Fe_{0.2}HPA$-7 catalyst was synthesized by introducing an accurately weighed portion of an iron wire into a standard catalyst solution. The solution was boiled for 40−50 min until the complete dissolution of the wire. The solution was cooled and left to stand for 24 h; within this time, a certain amount of an orange precipitate was formed; upon the repeated boiling of the solution for 15 min, the precipitate dissolved. After cooling, the solution volume (20 mL) was controlled and the E value was measured.

The synthesis procedure for the $Fe_{0.1}HPA$-7 catalyst was similar to that for the $Fe_{0.2}HPA$-7 catalyst. After preparing the solution and controlling the solution volume (20 mL), the E value was determined.

The $Cr_{0.2}HPA$-7 catalyst was prepared using a weighed portion of CrO_3, which was dissolved in a given volume of a standard catalyst solution; after that, a calculated amount of a 10 M hydrazine hydrate solution required for the reduction of Cr(VI) to Cr(III) was added to the resulting solution without the reduction of the HPA-7. The solution was boiled for 5 min and

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[1] This product was synthesized by the condensation of phthalic and tetrachlorophthalic anhydrides with urea and $CoCl_2$ and the subsequent sulfonation of the resulting mixture of phthalocyanines.

then cooled; the volume (20 mL) was controlled, and the E value was measured.

Measurement Procedure for the Redox Potentials of Catalyst Solutions

Redox potentials E of the oxidized and reduced catalyst solutions were determined at room temperature on an InoLab pH 730 pH meter (Wissenschaftlich-Technische Werkstatten GmbH, Germany) using a SenTix ORP Pt combination electrode. The constancy of E was achieved within 1 min with an accuracy of up to ± 0.001 V. In this study, E is given relative to a normal hydrogen electrode (NHE).

Butylene Reaction (I)

The butylene reaction (interaction of *n*-butylene with a Pd(II) + MeHPA-7 solution) was studied at atmospheric pressure in a 170-mL thermostated shaken glass reactor, which is referred to as a catalytic duck. Similarly to the procedure described in detail in [23], initially, the reactor containing 20 mL of the catalyst was blown with C_4H_8 without bubbling; after that, the reactor was connected to a burette filled with *n*-butylene, and shaking was started. At a reactor shaking frequency of 1200 min^{-1}, the reaction occurred in the kinetic region. Below, in Figs. 1−6, the time dependences of *n*-C_4H_8 volumes absorbed by Pd(II) + MeHPA-7 solutions are shown. Reaction rate was determined in the initial portion of the kinetic curve, where the rate was constant. The selectivity of the butylene reaction was controlled by gas−liquid chromatography (GLC) on a Khromos GKh-1000 chromatograph (Russia) [23].

Catalyst Regeneration by Reaction (II)

Solutions of Pd(II) + MeHPA-7 catalysts were regenerated in a thermostated autoclave with a glass insert at temperatures of 160−190°C and $P_{O_2} = 0.4$ MPa as described in [13] under stirring; additional conditions are described in the captions to the tables.

RESULTS AND DISCUSSION

In studying the effect of corrosion products of special steels on the efficiency of a homogeneous two-component catalyst for MEK synthesis, the catalyst based on $Ni_{0.2}HPA$-7 was studied first. It should be noted that the E value of the 0.25 M standard (parent) HPA-7 solution is 1.090 V; however, after the introduction of 0.2 mol of Ni per mole of HPA-7, the potential decreased to 1.044 V. After the holding of the prepared solution (20 mL) for 3 days, traces of a light brown precipitate (vanadium compound) appeared at the bottom of the glass; upon boiling, the precipitate dissolved. After that, the $Ni_{0.2}HPA$-7 catalyst (Pd and

Butylene volume, mL
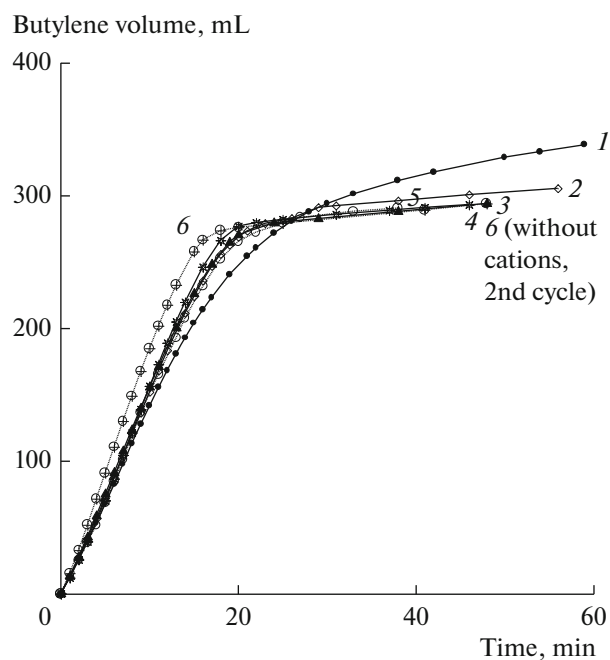
Fig. 1. Oxidation of *n*-butylene to MEK in the presence of the $Ni_{0.2}HPA-7$ catalyst, five cycles. Curve number corresponds to cycle number; (*6*) the standard catalyst without cations. Conditions: $V_{cat} = 20$ mL and $T = 60°C$ (see Table 1).
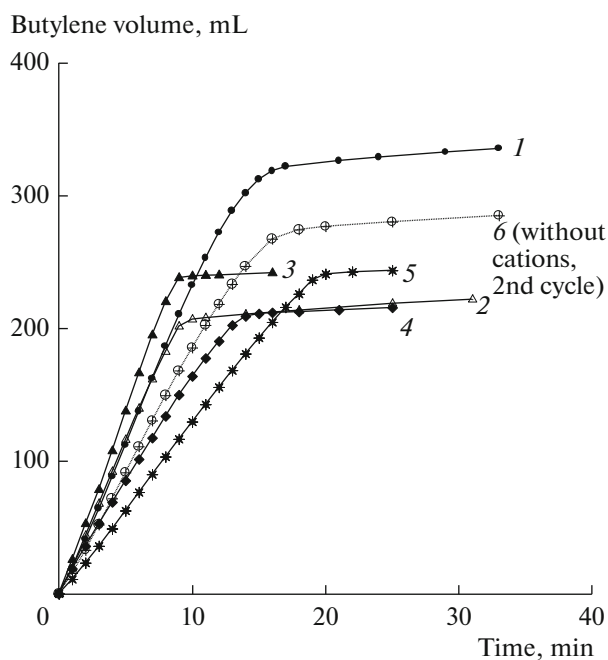
Fig. 2. Oxidation of *n*-butylene to MEK in the presence of the $Fe_{0.2}HPA-7$ catalyst, five cycles. Curve number corresponds to cycle number; (*6*) the standard catalyst without cations. Conditions: $V_{cat} = 20$ mL and $T = 60°C$ (see Table 2).

Pc concentrations are given in the tables) was tested in five cycles of the butylene reaction. The results are shown in Table 1 and Fig. 1.

The tests of the above catalyst showed that the introduction of Ni leads to a deterioration of the stability of palladium in solution. In the case of the complete reduction of the catalyst solution based on $Ni_{0.2}HPA-7$, even in the first cycle, a portion of palladium precipitates on the reactor walls and the electrodes in the form of a black precipitate during the measurement of the *E* value. It can be concluded that Ni^{+2} competes with Pd(0) for the coordination site in

the cobalt Pc molecule. However, after the oxidation of the reduced catalyst solution (regeneration) at 190°C for 30 min, the catalyst activity in reaction (I) in the next four cycles remained the same as in the first cycle. This means that the entire Pd metal precipitated in the form of a "mirror" from the reduced catalyst solution based on $Ni_{0.2}HPA-7$ with a significant decrease in *E* to a value of $E_{red} = 0.506-0.510$ V during the butylene reaction (Table 1) undergoes complete dissolution during oxygen reaction (II) with an increase in E_{oxid} of the solution to 1.000 V.

Table 1. Testing of the $Ni_{0.2}HPA-7$ catalyst in five cycles of n-C_4H_8 oxidation to MEK*

Cycle number	E_0, V	τ_{but}, min	V_{but}, mL (Δm)	W_{but} average within 10 min, mL/min	E_{red}, V	τ_{oxyg}, min	E_{oxid}, V	Notes
1	1.044	59	320 (5.43)	14.1	0.510	40	1.000	After the test, there was a precipitate of Pd_{met} on the duck; the precipitate dissolved in the oxidized catalyst
2	1.000	56	288 (4.56)	15.2	0.509	40	0.978	"
3	0.978	48	279.5 (4.40)	15.6	0.506	30	1.000	"
4	1.000	41	278.6 (4.46)	15.6	0.506	30	0.979	"
5	0.979	37	279.3 (4.48)	15.1	0.510	30	0.980	"

* Conditions: $V_{cat} = 20$ mL, $[Pd] = 6 \times 10^{-3}$ M, $[Pc] = 9 \times 10^{-3}$ M, $T_{but} = 60°C$, and $T_{oxyg} = 190°C$.
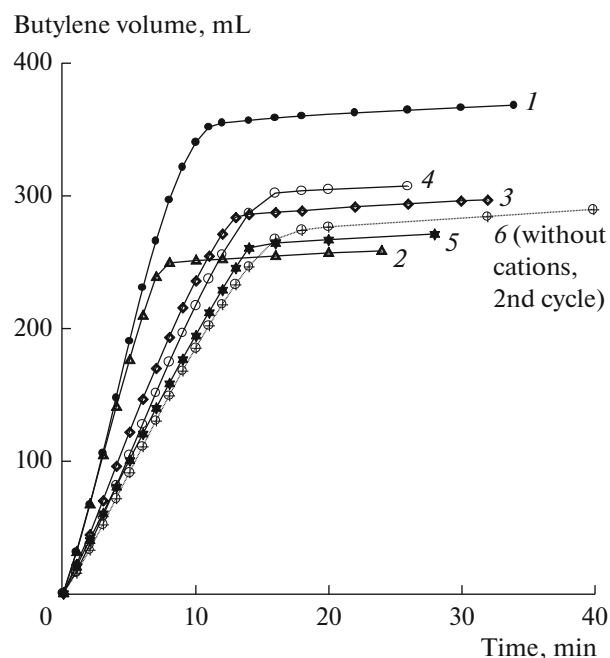
Butylene volume, mL

Fig. 3. Oxidation of *n*-butylene to MEK in the presence of the $Fe_{0.1}HPA-7$ catalyst, five cycles. Curve number corresponds to cycle number; (*6*) the standard catalyst without cations. Conditions: $V_{cat} = 20$ mL and $T = 60°C$ (see Table 3).

Fig. 4. Oxidation of *n*-butylene to MEK in the presence of the $Cr_{0.2}HPA-7$ catalyst, five cycles. Curve number corresponds to cycle number; (*6*) the standard catalyst without cations. Conditions: $V_{cat} = 20$ mL and $T = 60°C$ (see Table 4).

Analyzing the data in Table 1, it should be noted that, with a decrease in the catalyst regeneration time (τ_{oxyg}) from 40 to 30 min, the degree of oxidation of the catalyst (E_{oxid}) remains almost unchanged. Therefore, it can be concluded that, at a temperature of 190°C, the time of 30 min is quite sufficient for the complete oxidation of the reduced form of the catalyst.

The oxidation potential of the next catalyst solution based on $Fe_{0.2}HPA-7$ ($E = 1.040$ V) is close to the E value of the $Ni_{0.2}HPA-7$ catalyst ($E = 1.044$ V); this fact is attributed to the almost identical decrease in the acidity of the solutions upon the introduction of Ni and Fe cations in identical concentrations into the solutions, rather than to the nature of these cations. After repeated boiling, the $Fe_{0.2}HPA-7$ solution was left to stand for 4 days more. A small amount of a brown jelly-like precipitate—apparently, Fe(III) hydroxides—was observed on the bottom of the beaker. The catalyst, together with this precipitate, was tested in five cycles of the butylene reaction; the results are shown in Table 2 and Fig. 2.

Even after the first cycle, the jelly-like precipitate underwent dissolution and was not formed again; however, traces of a light brown precipitate (apparently, V_2O_5) were observed; it precipitated only from the solution of the regenerated catalyst. During the tests, the mass of the solid phase did not increase.

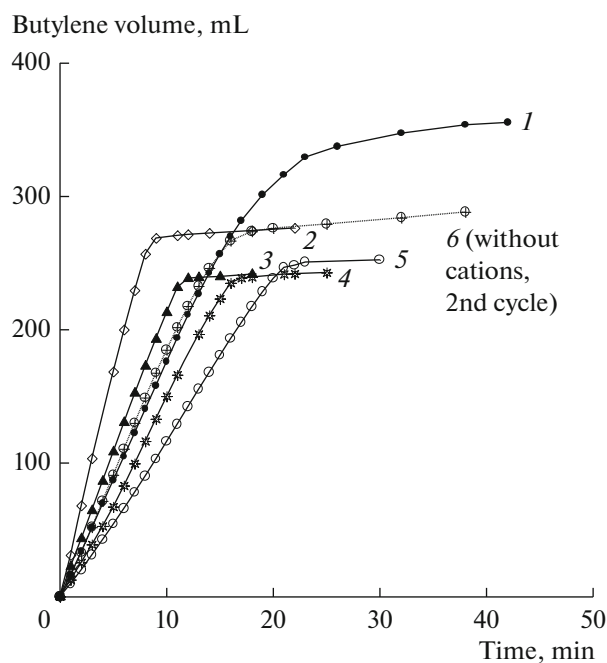It should be noted that the amount of metallic palladium precipitated from the reduced solution based

on $Fe_{0.2}HPA-7$ is larger than the amount precipitated from the $Ni_{0.2}HPA-7$ catalyst; that is, Fe(III) cations decrease the stability of reduced palladium more significantly. The data in Table 2 suggest that, in the presence of $Fe_{0.2}HPA-7$, the E value of the maximally reduced catalyst solution is 0.516−0.521 V, which is slightly higher than the E value in the case of $Ni_{0.2}HPA-7$.

To obtain more data on the required duration of the oxygen reaction, the regeneration time of this catalyst was decreased from 30 to 20 min. According to the E_{oxid} value, within 20 min, at 190°C, this catalyst obviously does not have time to undergo oxidation to a fairly high degree ($E_{oxid} = 0.950−0.960$ V); therefore, Pd does not entirely return to the solution. This fact represents the decrease in the average butylene reaction rate W_{but} in the fourth and fifth cycles (Table 2).

To determine the MA concentration of iron in solution, the catalyst containing a 2 times lower amount of iron cations ($Fe_{0.1}HPA-7$) was also tested. After preparation of the solution, it was left to stand for 2 days; no precipitates were formed; only a slight turbidity in the solution was observed. This catalyst was used in five cycles of n-C_4H_8 oxidation (Table 3, Fig. 3).

In the first two cycles of the butylene reaction, the catalyst operated at an extremely high rate, which exceeded the rate of the reaction with a solution without additional cations (second cycle for the standard catalyst solution is shown by a dashed line in Fig. 3,
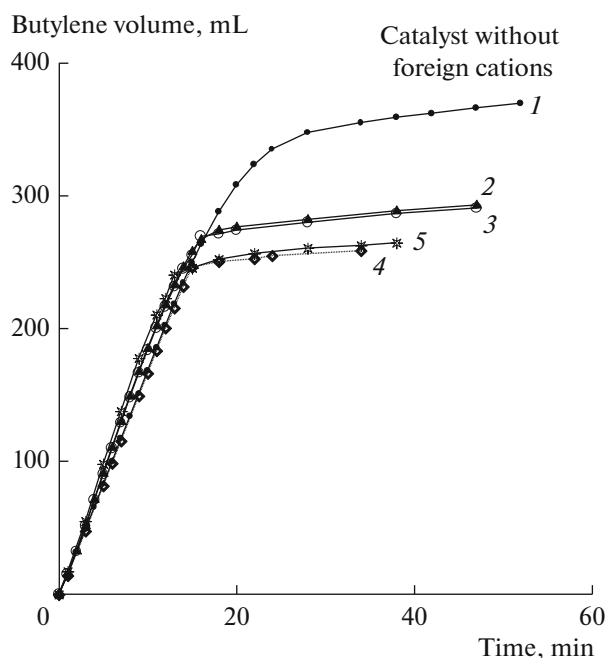
Fig. 5. Oxidation of *n*-butylene to MEK in the presence of the HPA-7 catalyst (without additional cations), five cycles. Curve number corresponds to cycle number. Conditions: $V_{cat} = 20$ mL and $T = 60°C$ (see Table 5).

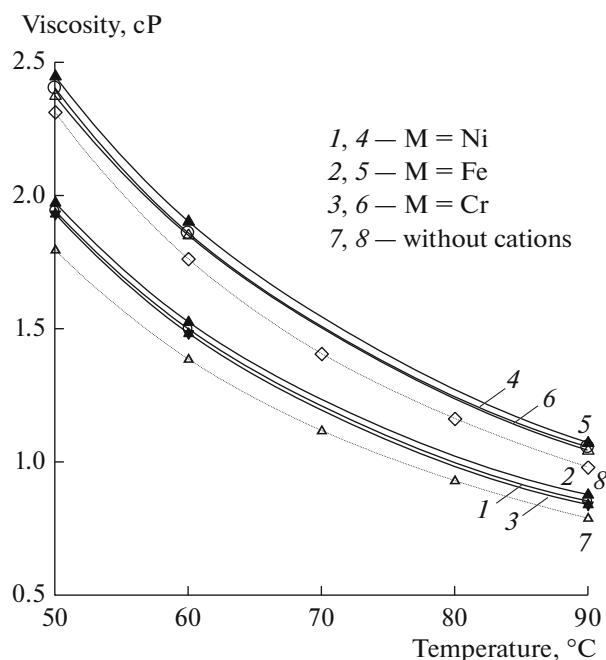**Fig. 6.** Temperature dependence of the viscosity of 0.25 M solutions of catalysts: (solid curves) $M_{0.2}HPA-7$ (containing corrosion products) and (dotted line) free HPA-7 at the different degrees of reduction: $m =$ (curves *1–3, 7*) 0.35 and (curves *4–6, 8*) 6.10.

curve *6*). This high rate is attributed to the fact that iron cations displaced palladium from the Pd–cobalt Pc complex; it is known that a Pd aqua complex exhibits a significantly higher activity in the butylene reaction [24]. In the next cycles, the activity of the Fe$_{0.1}$HPA-7 catalyst, in common with the activity of Fe$_{0.2}$HPA-7, systematically decreased (compare Figs. 2 and 3).

The results obtained upon an increase in the regeneration time of the catalyst based on Fe$_{0.1}$HPA-7 from

Table 2. Testing of the Fe$_{0.2}$HPA-7 catalyst in five cycles of *n*-C$_4$H$_8$ oxidation to MEK*

Cycle number	E_0, V	τ_{but}, min	V_{but}, mL (Δm)	W_{but} average within 10 min, mL/min	E_{red}, V	τ_{oxyg}, min	E_{oxid}, V	Notes
1	1.040	33	324.4 (5.23)	23.2	0.518	20	0.906	Before the test, there was a jelly-like precipitate in the solution. After the test, no Pd$_{met}$ was detected.
2	0.906	31	211.8 (3.48)	20.6	0.521	20	0.959	Before the test, there was a small amount of a precipitate.
3	0.959	16	236.2 (3.86)	23.9	0.520	20	0.917	Before the test, there was a small amount of a light precipitate. A Pd$_{мет}$ phase was observed on the duck.
4	0.917	25	207.3 (3.39)	16.3	0.519	20	0.963	Before the test, there was a small amount of a light precipitate. After reaction (I), there was a large amount of Pd$_{met}$; it did not entirely dissolve in the regenerated catalyst.
5	0.979	37	279.3 (4.48)	12.9	0.516	20	0.949	″

* Conditions: $V_{cat} = 20$ mL, $[Pd] = 6 \times 10^{-3}$ M, $[Pc] = 9 \times 10^{-3}$ M, $T_{but} = 60°C$, and $T_{oxyg} = 190°C$.

Table 3. Testing of the $Fe_{0.1}HPA$-7 catalyst in five cycles of n-C_4H_8 oxidation to MEK*

Cycle number	E_0, V	τ_{but}, min	V_{but}, mL (Δm)	W_{but} average with in 10 min, mL/min	E_{red}, V	τ_{oxyg}, min	E_{oxid}, V	Notes
1	1.066	34	357.3 (5.79)	33.9	0,518	20	0.966	The initial solution was homogeneous. After reaction (I), traces of Pd_{met} were observed.
2	0.966	24	250.6 (4.08)	25.1	0.515	30**	1.000	After reaction (I), traces of Pd_{met} were observed.
3	1.000	32	286.6 (4.65)	23.5	0.516	30	1.018	Before the test, the solution was homogeneous. After reaction (I), Pd_{met} was not detected.
4	1.018	26	268.8 (4.89)	21.7	0.516	30	0.982	There were traces of Pd_{met} in the reduced solution.
5	0.982	28	262.1 (4.23)	19.4	0.519	30	0.980	A considerable amount of Pd_{met}, especially upon MEK stripping, was detected.

* Conditions: V_{cat} = 20 mL, [Pd] = 6 × 10^{-3} M, [Pc] = 9 × 10^{-3} M, T_{but} = 60°C, and T_{oxyg} = 190°C.

** The oxygen reaction time is increased from 20 to 30 min.

20 to 30 min (Table 3) show that, within 30 min, at 190°C, the solution has time to undergo oxidation to a sufficiently high degree to achieve a value of E_{oxid} ~ 0.980 V. However, a longer regeneration time of the solution did not improve the stability of the palladium component of the catalyst. Initially—upon the introduction of Fe into the solution—the butylene reaction rate abruptly increases (compare curves *1* and *6* in Figs. 2 and 3); however, it gradually decreases from cycle to cycle owing to a decrease in the stability of Pd and losses of palladium in the form of metal precipitates on the equipment. In the presence of $Fe_{0.1}HPA$-7, the *E* value of the maximally reduced catalyst solution varies in a range of 0.515–0.519 V. The reduced solution of $Fe_{0.1}HPA$-7, in common with $Fe_{0.2}HPA$-7, releases a significant amount of metallic palladium after the fourth and fifth cycles.

Finally, the catalyst based on $Cr_{0.2}HPA$-7 was tested. It was found that, upon the introduction of 0.2 mol of Cr per mole of HPA-7, the *E* value is 1.081 V; that is, in the presence of chromium, the decrease in the *E* value (from the standard value of 1.090 V) is lower than the decrease in the case of nickel and iron cations. The $Cr_{0.2}HPA$-7 solution was left to stand for 3 days; it remained homogeneous. After that, it was tested in five cycles of the butylene reaction (Table 4, Fig. 4).

In the first cycle, the activity of the $Cr_{0.2}HPA$-7 solution in the butylene reaction is the same as the activity of HPA-7 without cations; it abruptly increases in the second cycle and then gradually decreases from cycle to cycle. The *E* value of the max-

imally reduced catalyst solution based on $Cr_{0.2}HPA$-7 lies in a range of 0.514–0.520 V.

An increase in the regeneration time of this catalyst from 20 to 30 min does not lead to the stabilization of the catalyst activity in reaction (I), because it is not oxidized to a sufficiently high degree within 30 min (to E_{oxid} > 0.98 V). The precipitation of Pd_{met} from the reduced catalyst is observed from the third cycle (Table 4).

Analysis of the data on the behavior of four different solutions of catalysts based on acid salts of transition metals suggests that the stability of palladium in the $Cr_{0.2}HPA$-7 catalyst solution is lower than that in the standard solution; however, the stability of Pd in the $Fe_{0.2}HPA$-7 solution is even worse than that in the Cr-containing catalyst.

Thus, the study has proven that the appearance of transition metal cations, which are corrosion products of special steels, in a homogeneous catalyst for MEK synthesis leads to a significant deterioration of the stability of the Pd(II) + HPA-7 catalyst. It accumulates iron-containing precipitates, which apparently are composed of iron(III) hydroxide and iron(III) vanadate $FeVO_4$. Transition metal cations are responsible not only for the initiation of precipitation, but also for a decrease in the stability of Pd(0) in the reduced catalyst, because they compete with palladium for the coordination site in the Pc ligand molecule and displace it from the Pd^0–Pc complex. This displacement leads to the formation of a Pd_{met} phase and a gradual decrease in the palladium concentration in the catalyst solution.

Table 4. Testing of the $Cr_{0.2}HPA$-7 catalyst in five cycles of n-C_4H_8 oxidation to MEK*

Cycle number	E_0, V	τ_{but}, min	V_{but}, mL (Δm)	W_{but} average with in 10 min, mL/min	E_{red}, V	τ_{oxyg}, min	E_{oxid}, V	Notes
1	1.081	42	342.5 (5.62)	17.6	0.520	20	0.988	Before the test, the solution was homogeneous After the test, Pd_{met} was not detected.
2	0.988	22	269.4 (4.40)	29.8	0.518	20	0.962	"
3	0.962	18	235.3 (3.85)	21.3	0.514	20	0.963	Before the test, there was a slight amount of a light precipitate. After the test, Pd_{met} was detected.
4	0.963	25	235.2 (3.82)	15.0	0.518	30**	0.976	Before the test, there was a slight amount of a light precipitate. Traces of Pd in the reduced solution were detected.
5	0.976	30	243.2 (3.98)	11.6	0.520	20	0.960	Slight turbidity in the patent solution was observed. After the test, Pd_{met} was detected.

* Conditions: V_{cat} = 20 mL, [Pd] = 6×10^{-3} M, [Pc] = 9×10^{-3} M, T_{but} = 60°C, and T_{oxyg} = 190°C.

** The oxygen reaction time is increased from 20 to 30 min.

An additional verification of the stability of palladium in the standard solution of the catalyst based on free HPA-7 (without additional introduction of M cations) in five cycles of butylene oxidation to MEK showed that this catalyst remains homogeneous. Metallic palladium does not precipitate from the reduced solutions (Table 5, Fig. 5); therefore, the activity of it in reaction (I) is constant. The maximally reduced catalyst based on free HPA-7 has E_{red} values in a range of 0.508–0.511 V.

It should be noted that a decrease in the time of reaction (II) for the standard catalyst from 30 to 20 min (Table 5) leads to a significant decrease in E_{oxid}. Therefore, it can be concluded that the catalyst regeneration time should be at least 30 min. In addition, in the first and second cycles, a negligible amount of a precipitate (apparently, V_2O_5) can be formed in the standard solution; subsequently, the mass of the precipitate does not increase (it was not filtered off).

According to the data on the effect of the corrosion products of special steels (transition metal cations) on the properties and stability of the homogeneous Pd(II) + HPA-7 ($H_{10}P_3Mo_{18}V_7O_{84}$) catalyst for the two-stage oxidation of n-butylene to MEK with oxygen, a number of important conclusions were drawn. First, the HPA-7 solution as the catalyst component actually exhibited an insufficient stability in the oxidized form of the catalyst (at 190°C after the oxygen reaction): during multicycle tests, a gradual accumulation of vanadium-containing precipitates was observed. Second, the palladium component of the catalyst—the complex of Pd^0 with a Pc ligand (Pd^0–Pc)—was unstable in the solution of the completely reduced catalyst at temperatures of 60–100°C. In this case, after reaction (I)

and at the MEK stripping stage, the formation of a palladium mirror was observed.

It was confirmed (Table 5, Fig. 5) that the catalyst was always unstable only in the presence of the corrosion products (M) in MA concentrations. The instability was evident as a systematic decrease in the catalyst activity in the butylene and oxygen reactions and as precipitation. Thus, at 190°C, the formation of precipitates from the oxidized form of the catalyst was observed; the precipitates entrained the M ions and a portion of vanadium from the solution; however, these precipitates never contained palladium. The precipitates gradually formed from the solution of the completely reduced form of the catalyst were composed entirely of palladium; at the same time, the corrosion products (M) and HPA-7 were quite stable and did not give precipitates from the reduced solutions in the entire temperature range of 20–190°C.

Here, it will be appropriate to mention the tests of the thermal stability of the catalysts that were conducted in studying the corrosion of special steels in HPA-x solutions [16]. Ni^{2+} cations do not change the thermal stability of the catalysts, whereas Cr^{3+} and, especially, Fe^{3+} cations (at $[Fe^{3+}] > 0.025$ M) significantly worsen this parameter. Cr^{3+} and Fe^{3+} cations initiate the formation of precipitates, which are mostly composed of vanadium compounds. These precipitates do not dissolve in the catalyst during cyclic operation; therefore, they lead to a decrease in the catalyst productivity, because it is the vanadium atoms in HPA-x solutions that undergo redox transformations: V(V) → V(IV) → V(V). As a consequence, it is necessary to periodically filter catalysts based on HPA-x and

Table 5. Testing of a catalyst based on HPA-7 (without additional metal cations) in five cycles of n-C_4H_8 oxidation to MEK*

Cycle number	E_0, V	τ_{but}, min	V_{but}, mL (Δm)	W_{but} average with in 10 min, mL/min	E_{red}, V	τ_{oxyg}, min	E_{oxid}, V	Notes
1	1.090	52	353.2 (5.70)	17.2	0.508	30	1.000	No precipitation was observed.
2	1.000	47	279.3 (4.49)	18.6	0.511	30	1.002	"
3	1.002	46	276.3 (4.44)	18.3	0.509	30	0.973	"
4	0.973	33	251.0 (4.10)	20.3	0.510	20*	0.963	Slight turbidity in the patent solution was observed. After reaction (I), Pd_{met} was not detected.
5	0.963	38	259.5 (4.21)	20.9	0.510	30	0.984	Slight turbidity in the patent solution was observed. No Pd_{met} was detected.

* Conditions: V_{cat} = 20 mL, [Pd] = 6×10^{-3} M, [Pc] = 9×10^{-3} M, T_{but} = 60°C, and T_{oxyg} = 190°C.
** The oxygen reaction time is increased from 20 to 30 min.

correct their composition by adding the lost portion of vanadium.

In separate experiments without introducing M cations into the solution, it was shown that the exposure of the standard Pd(II)+HPA-7 catalyst at 190°C for 2−4 h leads to precipitation. This feature is attributed to the fact that the parent catalyst solution already contained Fe^{3+} ions (~0.05 M) introduced with reagent-grade V_2O_5 during the synthesis of the HPA-7 solution as described in [12]; therefore, in the case of a long-term high-temperature exposure, even at low Fe^{3+} cation concentrations, the catalyst was unstable.

In corrosion studies conducted for many hours, a completely oxidized 0.25 M HPA-7 solution characterized by an extremely low pH value of about −0.25 and a high E value of 1.090 V was used. This solution, which exhibited the maximum corrosive activity, had the most significant destabilizing effect on the 12Kh18N10T steel sample that underwent the most severe corrosion and supplied Fe^{3+} cations to the solution [16].

The set of data on the activity of a MEK synthesis catalyst based on an HPA-7 solution in reactions (I) and (II) and on the corrosion of samples of special steels [16] has led to the conclusion that the composition of this catalyst is not optimum.

Changes in the Physicochemical Properties of Catalysts Containing Different Amounts of Corrosion Products

To determine the comprehensive effect of the corrosion products (M) on the state of a MEK synthesis catalyst, it was necessary to assess changes in the phys-icochemical properties of the catalyst in the presence of transition metal cations. To this end, for three samples of HPA-7-based catalysts containing different M cations, changes in the density and viscosity of the HPA-7 solution (key catalyst component) in the oxidized and reduced state were studied at different temperatures and degrees of reduction of HPA-7 (m = $[V(IV)]_\Sigma/[HPA-7]$) in accordance with the procedures described in detail in [14, 17]. The studied catalysts included samples based on $Ni_{0.2}H_{9.6}P_3Mo_{18}V_7O_{84}$, $Fe_{0.2}H_{9.4}P_3Mo_{18}V_7O_{84}$, and $Cr_{0.2}H_{9.4}P_3Mo_{18}V_7O_{84}$.

The measurement results (Tables 6−8) showed that the introduction of Ni^{+2}, Fe^{+3}, and Cr^{+3} cations in concentrations of 5×10^{-2} M into the standard catalyst solution does not lead to a significant change in the density of the solutions. In the presence of all these cations, the ρ value increases only slightly compared with that of the standard solution.

For the same three solutions containing transition metal cations, the viscosity was measured (Table 9). The temperature dependences of η for three oxidized (m = 0.35) and reduced solutions (m = 6.1) and for the standard catalyst solution without cations at identical degrees of reduction are shown in Fig. 6. It is evident that the viscosity of the solutions containing corrosion products of special steels increases somewhat more significantly (compared with the density) relative to the viscosity of the solution of free HPA-7. In this case, the nature of the cation does not have a fundamental effect on the η value; it is affected only by the concentration of corrosion products, i.e., transition metal cations. However, this effect cannot be considered significant, because the changes in η do not exceed 7−8%.

Table 6. Density (ρ, g/cm³) of 0.25 M $Ni_{0.2}H_{9.4}P_3Mo_{18}V_7O_{84}$ solutions on the degree of reduction (m) at different temperatures

Degree of reduction m	Temperature, °C				
	50	60	70	80	90
0.35*	1.682	1.675	1.668	1.662	1.659
0.35	1.685	1.680	1.673	1.666	1.663
2.12	1.689	1.686	1.675	1.669	1.665
4.22	1.691	1.688	1.676	1.671	1.666
6.10	1.692	1.689	1.678	1.672	1.667

* For the standard catalyst without M cations.

Table 7. Density (ρ, g/cm³) of 0.25 M $Fe_{0.2}H_{9.4}P_3Mo_{18}V_7O_{84}$ solutions on the degree of reduction (m) at different temperatures

Degree of reduction m	Temperature, °C				
	50	60	70	80	90
0.35*	1.682	1.675	1.668	1.662	1.659
0.35	1.686	1.681	1.674	1.668	1.663
2.12	1.690	1.686	1.677	1.672	1.666
4.22	1.692	1.690	1.678	1.674	1.667
6.10	1.694	1.691	1.679	1.675	1.668

* For the standard catalyst without M cations.

Table 8. Density (ρ, g/cm³) of 0.25 M $Cr_{0.2}H_{9.4}P_3Mo_{18}V_7O_{84}$ solutions on the degree of reduction (m) at different temperatures

Degree of reduction m	Temperature, °C				
	50	60	70	80	90
0.35*	1.682	1.675	1.668	1.662	1.659
0.35	1.685	1.680	1.673	1.666	1.662
2.12	1.690	1.685	1.676	1.670	1.665
4.22	1.692	1.688	1.678	1.673	1.667
6.10	1.693	1.690	1.679	1.674	1.667

* For the standard catalyst without M cations.

According to analysis of the data, it was concluded that the corrosion products of special steels change the main physicochemical properties of the Pd(II) + HPA-7 catalyst only slightly; therefore, their effect on these properties during long-term cyclic tests of the catalyst in reactions (I) + (II) can be neglected. However, the same is not true of the stability of the catalysts.

Analysis of the totality of the results of studying the stability, activity in reactions (I) and (II), and thermal stability of the Pd(II) + HPA-7 catalyst suggested that the HPA-7-based solution in the oxidized form is insufficiently stable in the presence of the MA concentrations (<0.1 M) of M, i.e., the corrosion products of special steels. The source of transition metal cations is the fittings of the pilot industrial plant for MEK synthesis. Hence, to synthesize a high-technology catalyst for the MEK process, it was necessary to *optimize* the final composition of HPA-x. The catalyst should preserve homogeneity and high oxidation capacity in the presence of MA concentrations of transition metals during pilot operation.

It was experimentally found that the stability of an HPA-x solution can be increased only by changing the solution composition in the direction of increasing the phosphorus content. As a consequence, a new solution based on HPA-7' of an optimized composition ($H_{11}P_4Mo_{18}V_7O_{87}$) was proposed instead of a standard solution based on HPA-7 ($H_{10}P_3Mo_{18}V_7O_{84}$).

The new Pd(II) + HPA-7' catalyst was fairly stable in the range of MA concentrations of M ions in both the oxidized (up to 190°C) and reduced form (at 60−100°C). However, at corrosion product concentrations exceeding the MA content (i.e., [M] > 0.1 M), precipitates in the catalyst solution still can be formed. In these cases, during cyclic tests, the precipitates were removed from the oxidized catalyst solution (after regeneration) by filtration to determine their weight and elemental composition. It was found that the precipitate was typically composed of the major portion of the corrosion products (M) and a small portion of vanadium in the form of mixed oxides. If the loss of vanadium exceeded 8−10% of the V content in the HPA-7' solution, then the catalyst composition was corrected with respect to vanadium. As a consequence, the filtering of the precipitates made it possible to clean the catalyst from the major portion of the corrosion products (M) if their concentrations were higher than the MA content. This filtering significantly facilitated the pumping of the catalyst solution through the closed loop of the pilot plant [18].

The problem of providing the stability of palladium in the reduced form of the new catalyst in the presence of M cations was solved by compensating for the loss of the Pc ligand, which was entrained from the solution by precipitates initiated by corrosion products and gradually burned out during exposure to an oxidizing medium at a high temperature (oxygen reaction at 180−190°C).

In tests on controlling the activity of the new catalyst in the butylene reaction, the loss of Pc in the solution was evident as an abrupt increase in the rate of reaction (I), after which a portion of palladium precipitated on the reactor walls as a black precipitate. The

Table 9. Temperature dependence of the density (ρ) of 0.25 M $M_{0.2}H_{9.6}P_3Mo_{18}V_7O_{84}$ (M = Ni, Fe, Cr) solutions at different degrees of reduction (*m*)

Degree of reduction *m*	Viscosity η, cP								
	temperature, °C								
	50			60			90		
	Ni	Fe	Cr	Ni	Fe	Cr	Ni	Fe	Cr
0.35*	1.7935	1.7935	1.7935	1.3836	1.3836	1.3836	0.7879	0.7879	0.7879
0.35	1.9402	1.9715	1.9290	1.4970	1.5231	1.4810	0.8510	0.8757	0.8339
6.10	2.4004	2.4451	2.3718	1.8573	1.9008	1.8490	1.0542	1.0704	1.0415

* For the standard catalyst without M cations.

precipitated Pd readily returned to the solution upon contacting with the oxidized form of HPA-7'. After the addition of Pc, palladium was stabilized in the solution; it did not precipitate from the reduced catalyst as long as Pc was present in it. The described method of returning palladium from the Pd_{met} phase to the solution was used in the optimization of the MEK process technology on a pilot industrial plant, where the butylene feeding was periodically ceased (if necessary) and the oxidized catalyst solution (with high E_{oxid}) circulated in the closed loop of the pilot plant. During this procedure, Pd_{met} was oxidized with HPA and passed from the equipment walls into the catalyst solution; as a consequence, the catalyst activity returned to the initial value [18].

Eventually, the studies have shown that the change in the composition of a homogeneous catalyst for MEK synthesis from Pd(II) + HPA-7 to Pd(II) + HPA-7' has made it possible to abruptly decrease the catalyst sensitivity to the presence of corrosion products (Me). As a consequence, according to our estimates, the precipitation rate decreases by about 300–350 times. Small amounts of precipitates can be formed only in the case of a long-term operation of the catalyst (over several months). It is the catalyst of the optimized composition based on a solution of HPA-7' or an acid sodium salt of HPA-7' ($Na_{1.2}$HPA-7') that was patented as a homogeneous two-component catalyst for the MEK process [20, 21].

It has been confirmed that the oxidation capacity of the Pd(II) + HPA-7' catalyst is clearly proportional to the V(V) concentration in the solution, i.e., the degree of reduction *m*. The basic dependences of *E* and pH on *m* for the optimized catalyst based on HPA-7' and the $Na_{1.2}$HPA-7' acid sodium salt, compared with the dependences of a standard HPA-7 solution, are shown in Fig. 7.

It is evident that the *E* values of the HPA-7 and HPA-7' solutions are almost identical, whereas the *E* value of the $Na_{1.2}$HPA-7' solution is considerably lower at the same *m* values. However, this version of the catalyst is of interest because the time of the oxygen reaction, the rate of which significantly increases

with a decrease in the acidity of the HPA-*x* solution [13], can be decreased in the presence of $Na_{1.2}$HPA-7'. Catalysts of this composition remain active in the butylene reaction for at least 15 cycles [20, 21].

One more important conclusion has been made from the studies: the stability of palladium in Pd(II) + HPA-7' solutions during multicycle tests can be provided even without introducing a Pc ligand. To this end, it is necessary to use solutions with a V(V) concentration that is strictly above the minimum allowable concentration. In this case, the $E_{(HPA-7'/H_mHPA-7')}$ value will remain higher than the $E_{(Pd^{2+}/Pd_{met})}$, value; this factor will provide a rapid electron transfer from Pd^0 to HPA-7' and hinder the aggregation of Pd^0 in the form of a Pd_{met} phase. It is difficult to determine exact
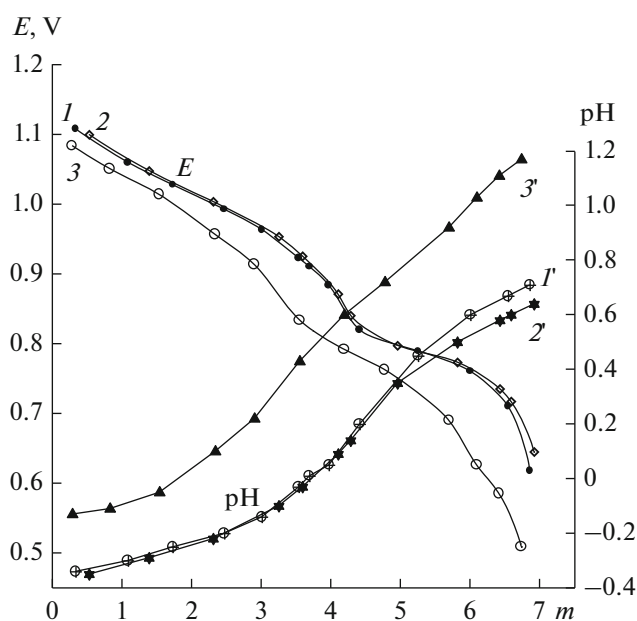

Fig. 7. Dependences of (curves *1–3*) *E* and (curves *1'–3'*) pH on *m* for 0.25 M solutions of catalysts containing (*1, 1'*) $H_{10}P_3Mo_{18}V_7O_{84}$, (*2, 2'*) $H_{11}P_4Mo_{18}V_7O_{87}$, and (*3, 3'*) $Na_{1.2}H_{9.8}P_4Mo_{18}V_7O_{87}$.

redox potential values of these systems. However, according to our experimental estimates, the stability region of reduced palladium lies in a range of the degree of reduction of HPA-7' of $0 > m > 5.6-5.7$; this feature restricts the E_{red} value of the HPA-x solution from below; it should necessarily remain >0.77 V. That is, if the Pd(II) + HPA-7' solution does not undergo rereduction during reaction (I), then it is highly probable that the stability of palladium in the homogeneous catalyst can be provided without a stabilizer.

CONCLUSIONS

Thus, the comprehensive study of the effect of equipment corrosion products (transition metal cations) on the physicochemical and catalytic properties and thermal stability of a homogeneous two-component Pd(II) + HPA-x catalyst developed for the two-stage oxidation of n-butylene to MEK with oxygen has made it possible to efficiently optimize the MEK process catalyst and eventually design a Pd(II) + HPA-7' catalyst. In the presence of this catalyst, the rate of precipitation initiated by the corrosion products of equipment made of special steels has been decreased by more than 300 times; it is this catalyst that has been used for the pilot industrial tests of the MEK process.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by M. Timoshinina