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# Hydroxylation of phenol by hydrogen peroxide catalyzed by heteropoly compounds in presence of glycerol as green solvent

K. Pamin[a,*], J. Połtowicz[a], M. Prończuk[b], S. Basąg[c], J. Maciejewska[a], J. Kryściak-Czerwenka[a], R. Tokarz-Sobieraj[a]

[a] Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Kraków, Poland
[b] Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland
[c] Jagiellonian University, Department of Chemistry, Ingardena 3, 30-060 Kraków, Poland

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ABSTRACT

Cobalt, manganese, and iron in cationic positions of the secondary structure of Mo- or W-Keggin type heteropolyanions were investigated in the liquid-phase oxidation of phenol in glycerol. Iron tungstophosphate series is the most active in this reaction, yielding catechol and hydroquinone. On the other hand, manganese and cobalt salts of heteropolyacids demonstrate higher catalytic activity in the degradation of phenol to $CO_2$ in comparison with iron tungstophosphates. It is the first time that glycerol is used as alternative "green" solvent in phenol oxidation reaction.

## 1. Introduction

Catalytic hydroxylation of phenol leads to catechol and hydroquinone which are important intermediates for production of fine chemicals. Total world production of phenol amounts to about 9 Mt per year [1]. Phenol is also dangerous pollutant in the natural environment because of its high toxicity and low biodegradability [2]. However, we are particularly interested in the oxidation of phenol to catechol and hydroquinone. It is industrially important reaction, because products have several important applications such as production of medicines, pesticides, perfumes, photographic film developer etc.

There are several technologies operated by chemical companies producing hydroquinone and catechol in hydroxylation of phenol. For example, Rhodia, Solvay owned company, uses dichloromethane in acid catalyzed phenol hydroxylation while in Enichem technology phenol is oxidized in the presence of TS-1 in dioxane and tetrahydrofuran as solvents [3]. Most of the currently running technologies use organic compounds as solvents in which other substances can dissolve and deliver heat. Many organic solvents are hazardous and toxic. They are volatile and may cause environmental threats by polluting the atmosphere. On the other hand, many natural products originated from the biomass utilization such as soy methyl ester, lactate ester, or glycerol are available. Glycerol is trihydroxy alcohol, nontoxic, biodegradable, and recyclable medium manufactured from renewable sources and is an attractive alternative to volatile organic solvents for catalytic reactions. The exchange of volatile organic solvents used in chemical processes for the environmentally friendly compound would have a great impact on the reduction of the use of organic solvents on industrial scale [4]. In the past glycerol was considered as expensive solvent. Due to the rapid expansion of biodiesel industry the availability of glycerol has improved significantly and the price dropped in 2010 to 0.50€ for 1 kg of 99.9% pure glycerol, thus making it an attractive "green" solvent.

The first example of the use of glycerol as a "green" solvent was reported in 2006 by Wolfson group [5] in asymmetric hydrogenation of prochiral β-keto esters and ketons. Both activity and enantioselectivity were high and competitive with the reactions in water. Another example of the use of glycerol as solvent is the simple reduction of benzaldehyde or ethyl acetoacetate with sodium borohydride followed by easy separation of the products [6]. However, no attempts to apply glycerol as solvent in the oxidation of phenol with hydrogen peroxide as oxidant in the presence of heteropoly compounds have been made so far.

Polyoxometalates are known as active and selective catalysts in different oxidation processes and they have received much attention in the field of catalytic oxidation [7]. They are metal–oxygen

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[*] Corresponding author. Tel.: +48 126395153; fax: +48 124251923.
*E-mail address:* ncpamin@cyf-kr.edu.pl (K. Pamin).

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cluster compounds possessing both acidic and redox properties which can be adjusted by a suitable choice of constituting elements. Introduction of a cation with variable oxidation state makes it possible to obtain new charge transfer complexes. Polyoxometalates are resistant to oxidative degradation and they continue to be active in oxidation reactions for a long time. It is important to emphasize that the complexes show multifunctionality in composition and physico-chemical properties and, as a consequence, it is possible to design the composition for a chosen reaction [8]. The nature of the aforementioned compounds assures their proper performance and high catalytic activity in homogeneous reactions.

Therefore, we propose, for the first time, the use of glycerol as an alternative "green" solvent for phenol oxidation reaction. The purpose of the present study is to explain how the application of glycerol as alternative solvent influences the catalytic activity of cobalt, manganese, and iron in cationic positions of the secondary structure of Mo- or W-Keggin type heteropolyanions in the liquid phase oxidation of phenol. We have prepared a series of cobalt, manganese, and iron salts of 12-tungstophosphoric (HPW) and 12-molybdophosphoric (HPMo) acids: $H_2M_{0.5}PX_{12}O_{40}$, $HMPX_{12}O_{40}$, and $M_3(PX_{12}O_{40})_2$, where M = Co, Mn, Fe, and X=Mo or W, and applied them as catalysts in the oxidation of phenol with hydrogen peroxide in glycerol. For comparison, the catalytic activities of HPW and HPMo have also been studied.

## 2. Experimental

### 2.1. Catalysts preparation

The series of cobalt and manganese dodecatungstophosphate or dodecamolybdophosphate were obtained as precipitate by mixing an aqueous solution of an appropriate amount of cobalt (II) or manganese(II) carbonate (Aldrich) with an aqueous solution of appropriate heteropolyacid. The solution was filtered and the mother liquor evaporated to dryness in the oven at 363 K. The following salts with varying number of metal cations in the heteropoly structure were synthesized: $H_2Co_{0.5}PW_{12}O_{40}$, $HCoPW_{12}O_{40}$, $Co_3(PW_{12}O_{40})_2$, $H_2Co_{0.5}PMo_{12}O_{40}$, $HCoPMo_{12}O_{40}$, $Co_3(PMo_{12}O_{40})_2$, $H_2Mn_{0.5}PW_{12}O_{40}$, $HMnPW_{12}O_{40}$, $Mn_3(PW_{12}O_{40})_2$, $H_2Mn_{0.5}PMo_{12}O_{40}$, $HMnPMo_{12}O_{40}$, $Mn_3(PMo_{12}O_{40})_2$. These samples are hereafter denoted by $H_2Co_{0.5}PW$, HCoPW, $Co_3PW$, $H_2Co_{0.5}PMo$, HCoPMo, $Co_3PMo$, $H_2Mn_{0.5}PW$, HMnPW, $Mn_3PW$, $H_2Mn_{0.5}PMo$, HMnPMo, $Mn_3PMo$, respectively.

The series of iron salts of dodecatungstophosphoric or dodecamolybdophosphoric acids were synthesized by mixing the stoichiometric amount of $FeCl_2$ with an aqueous solution of selected heteropolyacid. The resultant salts were dried in the oven at 363 K. The following salts with varying number of iron cation in the heteropoly structure were synthesized: $H_2Fe_{0.5}PW_{12}O_{40}$, $HFePW_{12}O_{40}$, $Fe_3(PW_{12}O_{40})_2$, $H_2Fe_{0.5}PMo_{12}O_{40}$, $HFePMo_{12}O_{40}$, $Fe_3(PMo_{12}O_{40})_2$, and for simplicity designated as $H_2Fe_{0.5}PW$, HFePW, $Fe_3PW$, $H_2Fe_{0.5}PMo$, HFePMo, $Fe_3PMo$, respectively.

### 2.2. Catalyst characterization

Fourier transform infrared (FT-IR) absorption spectra were recorded using Nicolet 6700 spectrometer under atmospheric conditions. Spectra of solid samples were recorded as KBr pellets in range of 4000–400 $cm^{-1}$ with resolution of 2 $cm^{-1}$ and collecting 64 scans.

Cyclic voltammograms were recorded in a three-electrode cell using 2.0 mm gold disc as the working electrode, platinum coil as auxiliary electrode and Ag/AgCl as reference electrode. All compounds were analyzed as 0.1 M water solutions in acetate buffer of pH 5.0 combined with HCl addition (sufficient to keep Keggin anion structure intact) as electrolyte. Prior to the measurements the solution was deaerated with argon to keep air-free atmosphere over the solution during the measurement.

The dehydration of ethanol was carried out in a conventional flow type reactor under atmospheric pressure. Typically, a 0.3 ml sample was placed in a quartz reactor. Ethyl alcohol was introduced into the helium stream (5.7% mole in He) by an evaporator–saturator set placed in a thermostat. The total flow rate of alcohol in the stream of the feed gas was 1.8 L/h. Before the test a catalyst was heated to 623 K at the rate 100 K/h and activated in a helium flow for 2 h. Catalytic tests were run at 498 K. The products were analyzed by means of the PerkinElmer 900 gas chromatograph equipped with FID detector and Porapak S column.

The liquid-phase oxidation of phenol was performed in a thermostated glass reactor equipped with condenser and stirrer. In a typical reaction, phenol (0.05 mole) and 30% aqueous $H_2O_2$ (0.05 mole) were dissolved in 2 ml of glycerol and the reaction mixture was heated on to 353 K with continuous stirring. The reaction started after the addition of $7.8 \times 10^{-6}$ mole of catalyst. After

**Table 1**
FTIR vibrations of iron, manganese, and cobalt dodecatungstophosphates or dodecamolybdophosphates.

| Vibration mode | HPW | $H_2M_{0.5}PW$ | HMPW | $M_3PW$ | HPMo | $H_2M_{0.5}PMo$ | HMPMo | $M_3PMo$ |
|---|---|---|---|---|---|---|---|---|
| | M=Fe | | | | M=Fe | | | |
| νas (P—$O_a$) | 1080 | 1080 | 1080 | 1080 | 1064 | 1064 | 1064 | 1064 |
| νas (X=Od) | 982 | 982 | 982 | 981 | 961 | 961 | 961 | 961 |
| $\nu_{as}$(X—$O_b$—X) | 891 | 889 | 889 | 892 | 870 | 869 | 870 | 871 |
| νas (X—Oc—X) | 797 | 800 | 799 | 804 | 782 | 782 | 783 | 784 |
| Vibration mode | HPW | $H_2M_{0.5}PW$ | HMPW | $M_3PW$ | HPMo | $H_2M_{0.5}PMo$ | HMPMo | $M_3PMo$ |
| | M=Mn | | | | M=Mn | | | |
| νas (P—$O_a$) | 1080 | 1080 | 1080 | 1080 | 1064 | 1063 | 1062 | 1061 |
| νas (X=Od) | 982 | 982 | 981 | 981 | 961 | 963 | 965 | 961 |
| $\nu_{as}$(X—$O_b$—X) | 891 | 890 | 893 | 895 | 870 | 877 | 880 | 881 |
| νas (X—Oc—X) | 797 | 804 | 807 | 806 | 782 | 795 | 799 | 796 |
| Vibration mode | HPW | $H_2M_{0.5}PW$ | HMPW | $M_3PW$ | HPMo | $H_2M_{0.5}PMo$ | HMPMo | $M_3PMo$ |
| | M=Co | | | | M=Co | | | |
| νas (P—$O_a$) | 1080 | 1080 | 1079 | 1079 | 1064 | 1064 | 1064 | 1062 |
| νas (X=Od) | 982 | 982 | 980 | 980 | 961 | 961 | 961 | 962 |
| $\nu_{as}$(X—$O_b$—X) | 891 | 889 | 894 | 895 | 870 | 870 | 870 | 880 |
| νas (X—Oc—X) | 797 | 804 | 807 | 808 | 782 | 782 | 782 | 799 |

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1 h of reaction time the oxidation was stopped and the products were analyzed using PerkinElmer Clarus 500 gas chromatograph equipped with FID detector and ZB 5MSi column. To analyze carbon dioxide formed in the oxidation of phenol in glycerol the reaction was performed in a stainless steel batch reactor of 50 ml volume in the conditions described above. Gas products were analyzed chromatographically using PerkinElmer Clarus 500 gas chromatograph equipped with FID detector connected with methanizer and ZB 5MSi column. Tar was analyzed by gravimetric method.

## 3. Results and discussion

The FT-IR spectra of iron, manganese, and cobalt dodecatungstophosphates or dodecamolybdophosphates are shown in Table 1. The samples were recorded as KBr pellets. Table 1 gathers spectra of parent tungstophosphoric acid and its Fe, Mn, and Co salts with 1, 2, or 3 protons substituted with the transition metal cation. Both heteropolyacids show four characteristic bands in the region 1100–700 $cm^{-1}$, which can be described as stretching vibration of $P—O_a$, $X{=}O_d$, $X—O_b—X$, and $X—O_c—X$ [9]. The oxygen atoms within Keggin anions can be identified as $O_a$—internal oxygen, $O_d$—terminal oxygen, $O_b$—corner sharing oxygen, and $O_c$—edge sharing oxygen [10]. The spectroscopic measurements show that the primary structure (Keggin) remains unaltered with the formation of the salt. The positions of $P—O_a$ and $W{=}O_d$, or $Mo{=}O_d$ bands are quite similar for all samples within each series. The bands associated with vibrations of bridging X—O—X chains show a slight shift toward higher frequencies upon stepwise introduction of the metal atom into the heteropoly structure. The changes of positions of the observed bands may be interpreted as a result of lowering the degree of hydroxylation of Keggin anions upon introduction of metal cations in the position of compensating cations [11]. Moreover, the shift toward higher wavenumber results from the shortening of the bond length between substituted metal and oxygen.

Figs. 1 and 2 present the results of voltammetric measurements for the series of cobalt salts of Mo- and W-based heteropolyacids, respectively. The wave shape and peak separation indicate reversibility. The upper figure presents voltammograms measured for molybdophosphoric acid. Two one-electron signals in the upper, oxidation wave are visible, and represent the 2-electron oxidation of the Keggin anion. In the corresponding bottom reduction wave two one-electron signals are also observed.

The substitution of protons for cobalt cations in the heteropoly structure results in two different effects observed in cyclic voltammetric measurements. In the presence of cobalt atom an additional, third signal appears in voltammograms (marked with arrows in Figs. 1 and 2). As the number of Co atoms in the heteropoly structure grows, the intensity of that signal increases gradually (Figs. S1, S2). Moreover, a shift to more negative potentials for $Co_xPW$ and $Co_xPMo$ series in comparison to parent heteropolyacids was also observed (Table 2). Similar observations can be made for manganese and iron catalysts.

Table 2 presents data of the position of signal I for dodecamolybdophosphate series and the position of signal II for dodecatungstophosphate series in both oxidation and reduction waves. HPMo is the reference sample for the molybdenum series of heteropoly salts with the position of signal I at 140.2 mV in the oxidation wave and 101.8 mV in the reduction wave (marked with asterisk in Fig. 1). For HPW which is the reference sample for tungsten series of catalysts the positions of signal II reach 42.2 mV in oxidation wave and −15.8 mV in reduction wave (marked with asterisk in Fig. 2). The introduction of transition metals into molybdophosphoric acid influences the position of signal I in cyclic voltammetry which in consequence lowers in comparison with the

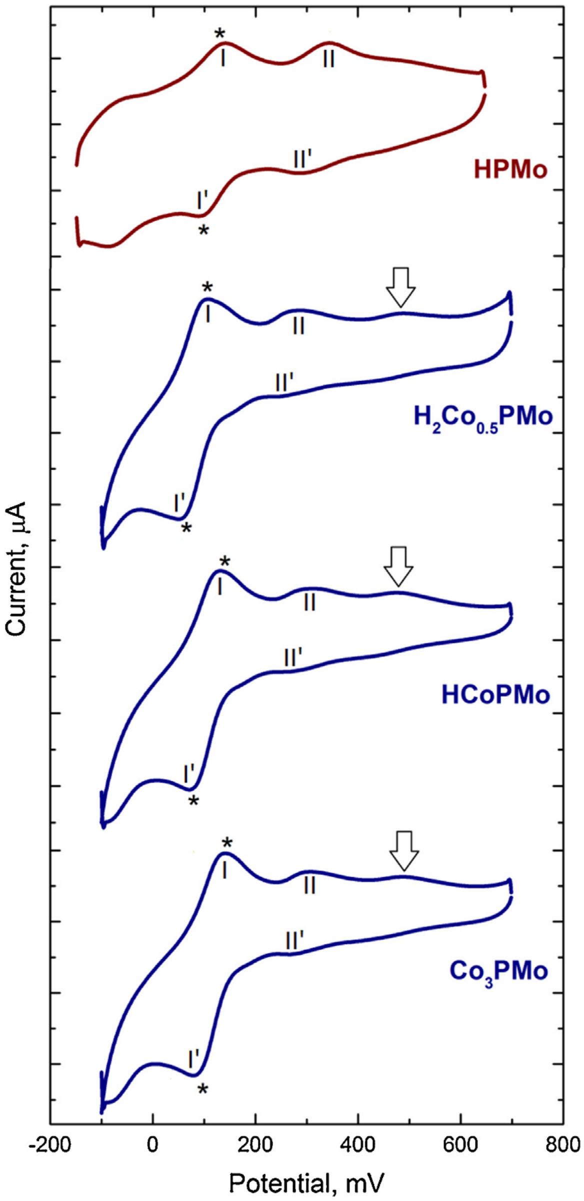

**Fig. 1.** Cyclic voltammograms of cobalt molybdophosphate series.

**Table 2**
Position of signal I for dodecamolybdophosphate series and the position of signal II for dodecatungstophosphate series.

Dodecamolybdophosphate series (signal I)

| Metal | Wave | HPMo | $H_2M_{0.5}PMo$ | HMPMo | $M_3PMo$ |
|---|---|---|---|---|---|
| Fe | Oxidation | 140.2 mV | 132.6 mV | 116.6 mV | 119.8 mV |
| | Reduction | 101.8 mV | 87.2 mV | 80.7 mV | 82.8 mV |
| Co | Oxidation | 140.2 mV | 98.2 mV | 124.1 mV | 133.1 mV |
| | Reduction | 101.8 mV | 61.1 mV | 80.8 mV | 89.0 mV |
| Mn | Oxidation | 140.2 mV | 123.2 mV | 129.4 mV | 128.4 mV |
| | Reduction | 101.8 mV | 74.6 mV | 80.2 mV | 79.2 mV |

Dodecatungstophosphate series (signal II)

| Metal | Wave | HPW | $H_2M_{0.5}PW$ | HMPW | $M_3PW$ |
|---|---|---|---|---|---|
| Fe | Oxidation | 42.2 mV | 34.2 mV | 32.5 mV | 30.2 mV |
| | Reduction | −15.8 mV | −19.0 mV | −20.1 mV | −17.8 mV |
| Co | Oxidation | 42.2 mV | 31.2 mV | 35.0 mV | 39.0 mV |
| | Reduction | −15.8 mV | −16.5 mV | −14.7 mV | −12.8 mV |
| Mn | Oxidation | 42.2 mV | 25.7 mV | 26.9 mV | 27.9 mV |
| | Reduction | −15.8 mV | −26.0 mV | −18.7 mV | −17.4 mV |

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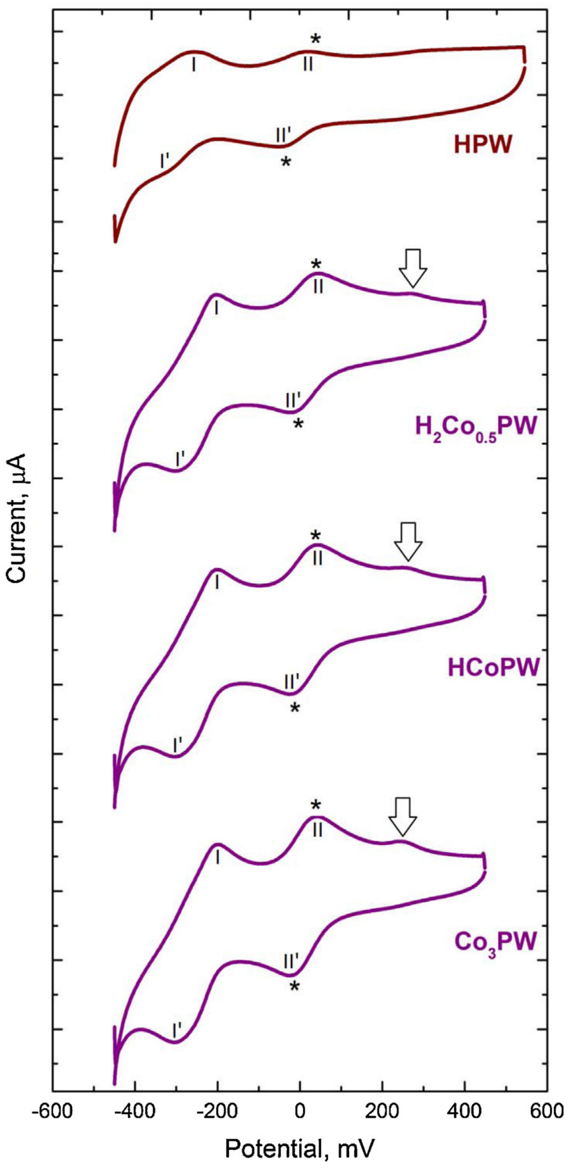


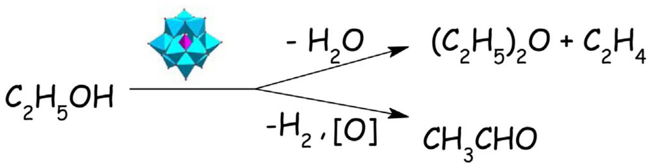
**Fig. 2.** Cyclic voltammograms of cobalt tungstophosphate series.

potential of HPMo. For tungstophosphoric acid-based catalysts a similar tendency as for the former catalytic series was observed.

Moreover, 1st one-electron reduction potentials for all the synthesized heteropoly salts were calculated and the results are gathered in Table 3. As can be seen, the values of reduction potentials gradually grow with the increase of number of metal atoms in heteropoly salt. The increase of reduction potential upon introduction of the cation into the secondary structure of Keggin anion results in easier oxidation and more difficult reduction with respect to parent heteropolyacids.

**Table 3**
1st one-electron reduction potentials of synthesized heteropoly salts.

| Dodecamolybdophosphate series (signal I) | | | |
|---|---|---|---|
| Metal | $H_2M_{0.5}PMo$ | HMPMo | $M_3PMo$ |
| Fe | 95.9 mV | 98.7 mV | 101.3 mV |
| Co | 79.7 mV | 102.5 mV | 111.1 mV |
| Mn | 98.9 mV | 104.8 mV | 103.8 mV |
| **Dodecatungstophosphate series (signal II)** | | | |
| Metal | $H_2M_{0.5}PW$ | HMPW | $M_3PW$ |
| Fe | 7.6 mV | 11.0 mV | 12.5 mV |
| Co | 7.4 mV | 11.1 mV | 13.5 mV |
| Mn | 0.4 mV | 4.1 mV | 5.3 mV |



**Scheme 1.** Dehydration of ethanol.

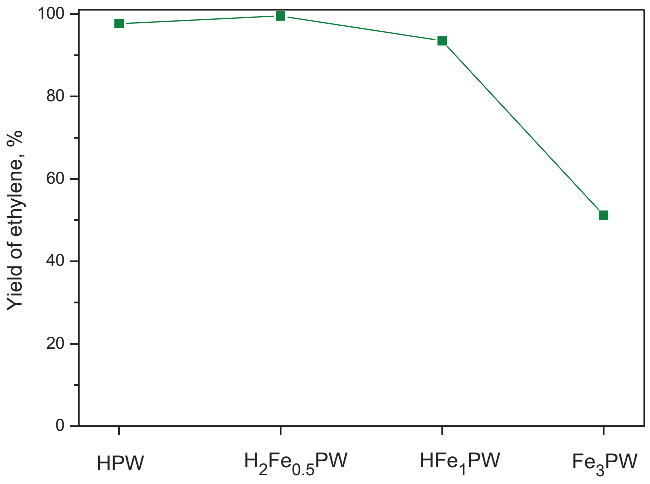


**Fig. 3.** Dehydration of ethanol for iron tungstophosphate series.

Heteropolyacids and their salts are active catalysts in alcohol dehydration [12–14]. The dehydration of alcohol is a model reaction to assess acid–base and redox properties of catalysts. During dehydration of alcohol and in the presence of acid centers, alcohol is transformed into ethers and olefins. In the presence of redox centers alcohol is converted via oxidative dehydrogenation pathway into aldehyde or ketone.

Catalytic tests were performed in a flow reaction system, in quartz reactor, under the atmospheric pressure at 498 K. All catalysts were activated in helium stream, at 623 K, for 2 h. Catalytic properties of all the heteropoly salts were studied in ethanol dehydration (Scheme 1).

Figs. 3 and 4 show the results of catalytic tests performed in the dehydration of ethanol for $Fe_xPW$ and $Fe_xPMo$ series, respectively. Fig. 3 demonstrates the catalytic results for $Fe_xPW$ series, where tungstophosphoric acid was compared with iron dodecatungstophosphates. The only reaction product for this catalytic series is ethylene. A gradual exchange of protons for iron atoms results in the decrease of acid strength. Therefore the neutral salt, $Fe_3PW$, shows the lowest activity in this reaction.

The substitution of tungsten for molybdenum has a major influence on the acidic properties of the studied catalysts. The catalysts of iron dodecamolybdophosphate series (Fig. 4) are substantially less active in dehydration of ethanol (small yield to ethylene) mainly due to their weaker acidic properties. Oxidative dehydrogenation, which is carried out on the redox centers, leads to the formation of acetaldehyde.

Cobalt tungstophosphates (Fig. S3) and manganese tungstophosphates (Fig. S4) as well as cobalt molybdophosphates (Fig. S5) and manganese molybdophosphates (Fig. S6) demonstrate a similar tendency in ethanol dehydration.

Synthesized catalysts were applied in the phenol oxidation (Scheme 2) in glycerol which is inert solvent in these reaction

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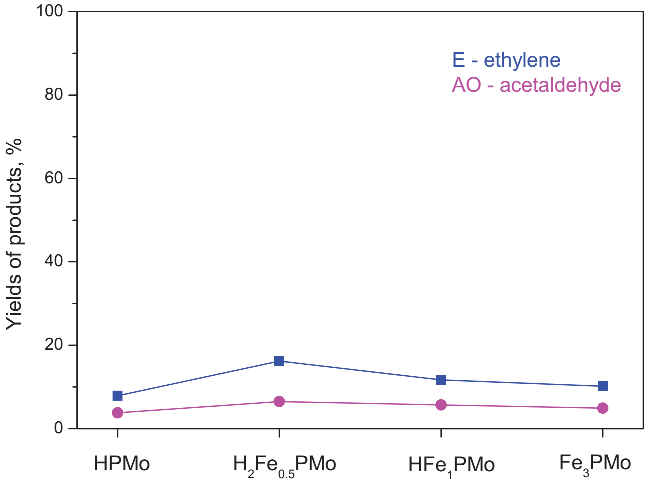
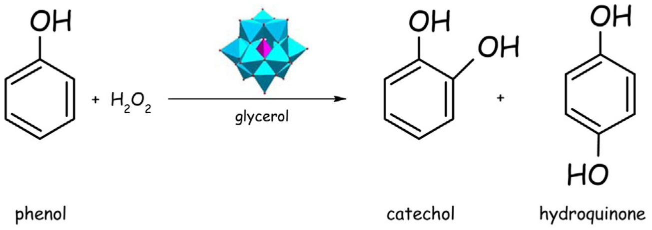


**Fig. 4.** Dehydration of ethanol for iron molybdophosphate series.



**Scheme 2.** Hydroxylation of phenol with hydrogen peroxide.

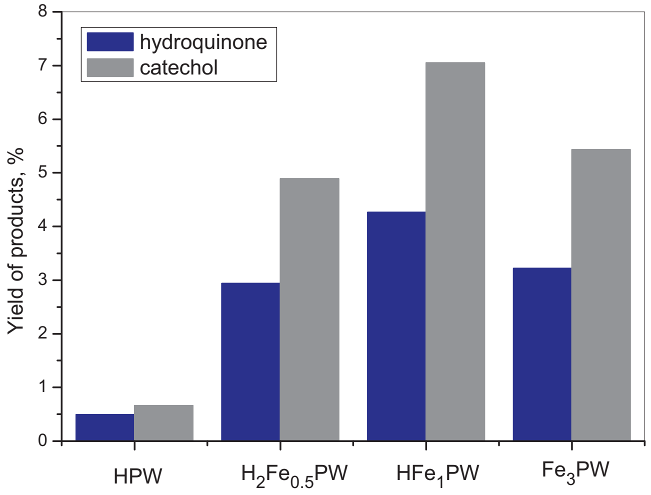


**Fig. 5.** Oxidation of phenol with iron tungstophosphate catalysts in glycerol.

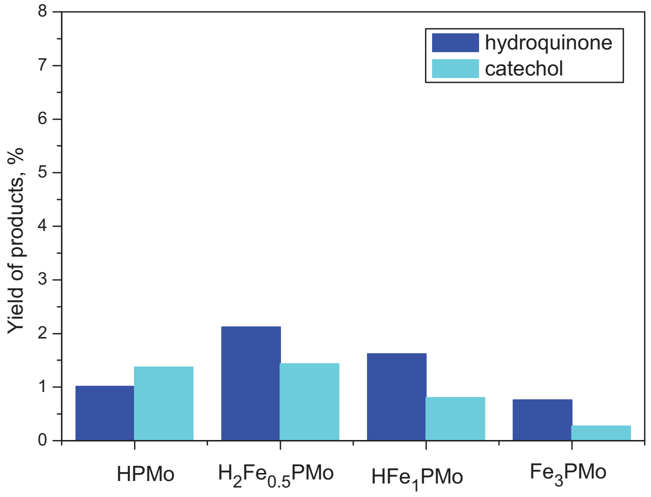


**Fig. 6.** Oxidation of phenol with iron molybdophosphate catalysts in glycerol.

conditions. Figs. 5 and 6 and S7–S10 present the results of catalytic tests in phenol oxidation with hydrogen peroxide and in glycerol solvent for iron, manganese, and cobalt tungstophosphates or molybdophosphates with respect to appropriate parent heteropolyacids. The catalytic activity of iron tungstophosphates is shown in Fig. 5. For the $H_2Fe_{0.5}PW$ catalyst, having the lowest content of iron in the catalytic series, the introduction of iron results in a significant increase of catalytic activity, which is accompanied by a small decrease of its acidic properties. For HFePW with one iron cation in the heteropoly structure, the increased number of iron cations causes a further increase of catalytic activity followed up by a progressive decrease of acid strength. Finally, for neutral salt $Fe_3PW$ the yield of desired products decreases in comparison with the FeHPW catalyst, which means that not only the metal centers but also the acidic properties are necessary to assure higher catalytic activity in this reaction. According to Ref. [15] phenol undergoes oxidation with $H_2O_2$ in the presence of Brønsted or Lewis acids catalysts. This is why iron tungstophosphates are more active in this reaction than iron molybdophosphates which have much weaker acidic properties (Fig. 6). The lowest activity for this catalytic series is observed for HPW.

Cobalt tungstophosphates (Fig. S7) and cobalt molybdophosphates (Fig. S8) show low catalytic activity in the oxidation of phenol. Similarly, manganese salts of tungstophosphoric acid (Fig. S9) and molybdophosphoric acid (Fig. S10) demonstrate low activity in the studied reaction. The catalysts of the $Mn_xPW$ series are the least active in the liquid-phase oxidation of phenol. It is not

**Table 4**
Catalytic activity of iron, cobalt, and manganese heteropoly salts in degradation of phenol to $CO_2$.

| Catalyst | Conversion of phenol [%] | Yield of [%] | | Catalyst | Conversion of phenol [%] | Yield of [%] | |
|---|---|---|---|---|---|---|---|
| | | $CO_2$ | tar[a] | | | $CO_2$ | tar[a] |
| HPW | 37.8 | 34.9 | 1.7 | HPMo | 39.3 | 35.0 | 1.5 |
| $H_2Fe_{0.5}PW$ | 46.5 | 36.8 | 1.9 | $H_2Fe_{0.5}PMo$ | 39.0 | 33.8 | 1.6 |
| HFePW | 44.6 | 31.5 | 1.8 | HFePMo | 27.4 | 24.1 | 0.9 |
| $Fe_3PW$ | 47.2 | 36.6 | 1.9 | $Fe_3PMo$ | 22.9 | 21.0 | 0.9 |
| $H_2Co_{0.5}PW$ | 43.1 | 39.3 | 1.6 | $H_2Co_{0.5}PMo$ | 40.6 | 37.0 | 1.7 |
| HCoPW | 52.1 | 48.1 | 2.5 | HCoPMo | 43.8 | 40.3 | 1.9 |
| $Co_3PW$ | 46.3 | 43.3 | 1.7 | $Co_3PMo$ | 45.0 | 41.0 | 1.9 |
| $H_2Mn_{0.5}PW$ | 43.9 | 41.1 | 1.6 | $H_2Mn_{0.5}PMo$ | 42.9 | 40.4 | 2.1 |
| HMnPW | 43.9 | 41.4 | 1.6 | HMnPMo | 40.7 | 36.9 | 1.7 |
| $Mn_3PW$ | 43.3 | 41.0 | 1.5 | $Mn_3PMo$ | 41.4 | 37.9 | 1.7 |

[a] Tar recalculated to $CO_2$.

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a surprise that iron catalysts are the most active in this reaction since in phenol oxidation by Fenton reagent ($H_2O_2 + Fe^{2+}$) iron plays a key role [16,17]. Preliminary DFT calculations for $H_2O_2$ activation on cation saturated by solvent ligands, which show that energetically favorable activation process occurs on Fe complex [18], additionally justify high activity of iron tungstophosphate salts in oxidation of phenol. This is why the majority of synthesized catalysts, except iron tungstophosphate series, show small catalytic activity in the oxidation of phenol.

Phenol is not only an important substrate to produce catechol and hydroquinone but it is also a dangerous pollutant. Many efforts have been taken to convert phenol into more biodegradable molecules [19,20]. It is important to stress that all the manganese- and cobalt-modified heteropoly compounds demonstrate higher catalytic activity in the degradation of phenol to $CO_2$ in comparison to iron catalysts. All catalysts show relatively high conversion of phenol in its degradation to $CO_2$ (Table 4). In fact, cobalt and manganese catalytic series are the most active in this reaction. Also, some polymeric species in the form of tar are present in the reaction mixture.

## 4. Conclusions

Catalytic investigations of phenol hydroxylation with $H_2O_2$ in glycerol as solvent demonstrated that glycerol can be an alternative to volatile organic solvents in phenol oxidation. The introduction of iron cation into HPW structure shows a substantial influence on the catalytic activity of heteropoly salts in the oxidation of phenol. Iron tungstophosphates are the most active among all investigated catalysts. Preliminary DFT calculations confirm the good catalytic performance of Fe complex [18]. However, iron tungstophosphates are also more active in this reaction than iron molybdophosphates due to much stronger acidic properties of the former catalytic series. The substitution of protons for iron atoms diminishes the acidic properties of heteropoly salts, necessary for their high catalytic activity. On the other hand, the introduction of additional iron cations results in the appearance of new catalytic centers in the studied reaction, increasing catalytic activity. Similar catalytic activities were demonstrated by industrial catalysts (Rhone Poulenc, Brichima, Enichem) [15]. Mn and Co salts of heteropolyacids are active catalysts of phenol degradation to carbon dioxide.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2015.03.003.

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