



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



K. Pamin<sup>a,\*</sup>, J. Połtowicz<sup>a</sup>, M. Prończuk<sup>b</sup>, S. Basąg<sup>c</sup>, J. Maciejewska<sup>a</sup>,  
J. Kryściak-Czerwenka<sup>a</sup>, R. Tokarz-Sobieraj<sup>a</sup>

<sup>a</sup> Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Kraków, Poland

<sup>b</sup> Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland

<sup>c</sup> 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<sub>2</sub> in comparison with iron tungstophosphates. It is the first time that glycerol is used as alternative “green” solvent in phenol oxidation reaction.

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## 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 ketones. 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

\* Corresponding author. Tel.: +48 126395153; fax: +48 124251923.

E-mail address: [ncpamin@cyf-kr.edu.pl](mailto:ncpamin@cyf-kr.edu.pl) (K. Pamin).

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  $4000\text{--}400\text{ cm}^{-1}$  with resolution of  $2\text{ cm}^{-1}$  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			
$\nu_{as}(P-O_a)$	1080	1080	1080	1080	1064	1064	1064	1064
$\nu_{as}(X=O_d)$	982	982	982	981	961	961	961	961
$\nu_{as}(X-O_b-X)$	891	889	889	892	870	869	870	871
$\nu_{as}(X-O_c-X)$	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			
$\nu_{as}(P-O_a)$	1080	1080	1080	1080	1064	1063	1062	1061
$\nu_{as}(X=O_d)$	982	982	981	981	961	963	965	961
$\nu_{as}(X-O_b-X)$	891	890	893	895	870	877	880	881
$\nu_{as}(X-O_c-X)$	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			
$\nu_{as}(P-O_a)$	1080	1080	1079	1079	1064	1064	1064	1062
$\nu_{as}(X=O_d)$	982	982	980	980	961	961	961	962
$\nu_{as}(X-O_b-X)$	891	889	894	895	870	870	870	880
$\nu_{as}(X-O_c-X)$	797	804	807	808	782	782	782	799

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