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A green, reusable and highly efficient solid acid catalyst for the oxidation of aldehydes to the corresponding carboxylic acids using H₂O₂ and KMnO₄:H₅PV₂Mo₁₀O₄₀ (10-molybdo-2-vanadophosphoric heteropolyacid)

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Abstract: H₅PV₂Mo₁₀O₄₀-catalyzed oxidation of aromatic aldehydes to the corresponding carboxylic acids using hydrogen peroxide and KMnO₄ as oxidants under mild conditions is reported. This system provides an efficient, convenient and practical method for the oxidation of aromatic aldehydes. In this work, differences between Keggin and Well–Dawson type polyoxometalates are addressed in term of relative stability, hardness and acidity.

Keyword: heteropolyacids; aldehydes; carboxylic acids; microwave irradiation; polyoxometalates.

INTRODUCTION

The catalytic function of heteropolyacids (HPAs) and related polyoxometalate compounds has attracted much attention, particularly over the last two decades.^{1–4} In this context, heteropolyacids (HPAs) are promising catalysts. A common and important class of these acids and those used in the majority of catalytic applications are Keggin compounds of the general formula H_nXM₁₂O₄₀ (X = P, Si, As, Ge or B; M = Mo and/or W).⁵ These solid acids are usually insoluble in non-polar solvents but highly soluble in polar ones. They can be used in bulk or supported forms in both homogeneous and heterogeneous systems. Furthermore, these HPAs have several advantages, including high flexibility in the modification of the acid strength, ease of handling, environmental compatibility, non-toxicity, and experimental simplicity.⁶ Keggin type polyoxoanions have been widely studied as homogeneous and heterogeneous catalyst for the oxidation of organic compounds.⁷

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Another catalytically important subclass of the Keggin compounds are the mixed vanadium (V) substituted HPAs of the general formula $H_{3+n}PV_nM_{12-n}O_{40}$ ($M = Mo$ and W ; $n = 1$ to 6). These compounds exhibit high activity in acid–base type catalytic reactions; hence, they are used in many catalytic areas as homogeneous and heterogeneous catalysts. The most well known of these HPAs is $H_5PV_2Mo_{10}O_{40}$.

In continuation of ongoing research^{8–12} on the syntheses and application of heteropolyacids in organic syntheses and due to the importance of derivatives of aldehydes in chemical processes, the applicability of HPA for efficient oxidation of aldehyde to the corresponding carboxylic acids is reported herein. Ishii and co-workers reported a number of interesting reactions catalyzed by transition metal-substituted heteropolyacids, including oxidation of aldehydes to carboxylic acids.¹³ Shimizu and co-workers showed how product selectivity and activity depend on the composition of the heteropolyanion and the type of counter cations as well as the support surface area.¹⁴ In addition, they emphasized that pore size distribution is very important. Mizuno and co-workers examined the oxidation of octanal by O_2 with both nickel- and iron-containing heteropolyacids.¹⁵ Zamaraev and co-workers reported the catalytic properties of several cobalt-containing heteropolyanions, *viz.* tetra-alkylammonium salts of $PW_{11}CoO_{39.5}$ and $CoW_{12}O_{40.6}$, in alkene epoxidation by dioxygen in the presence of *iso*-butyraldehyde, under ambient conditions.¹⁶ The mechanism and the catalytic activity of transition metal-substituted heteropolyacids have been speculated since 1970 and later on, the propensity of them to bind with molecular oxygen and the role of such dioxygen-activated species in the oxidation of organic substrates was explored.¹⁷

Microwave heating has been used for a wide variety of applications, including the rapid synthesis of organic compounds.^{18,19} Now, a very efficient and simple method for the oxidation of aldehydes to the corresponding carboxylic acids using H_2O_2 and $KMnO_4$ as the oxidizing reagent and catalyzed by mixed vanadium (V)-substituted HPAs under mild conditions is reported.

EXPERIMENTAL

All reagents and solvents used in this work are available commercially (Merck) and used as received, unless otherwise indicated. Previously reported methods were used to purify the aldehydes.²⁰ The preparation of the $H_5PV_2Mo_{10}O_{40}$ catalyst and other mixed heteropolyacids and salts were based on a literature procedure, with modifications as reported below.²¹ The acids of $[NaP_5W_{30}O_{110}]^{14-}$, $[P_2W_{18}O_{62}]^{6-}$ and $[P_2Mo_{18}O_{62}]^{6-}$ were prepared according to published methods and were identified by infrared spectroscopy.²² The 1H -NMR spectra were recorded on a Bruker 100 MHz Aspect 3000 FT-NMR instrument. The IR spectra were recorded on a Buck 500 scientific spectrometer (KBr pellets).

Preparation of $H_5PV_2Mo_{10}O_{40}$ ²¹

Sodium metavanadate (12.2 g, 100 mmol) was dissolved by boiling in 50 mL of water and then mixed with (3.55 g, 25 mmol) of Na_2HPO_4 in 50 mL of water. After the cooling the

solution, concentrated sulphuric acid (5 mL, 17 M, 85 mmol) was added, whereby a red colour developed. $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (60.5 g, 250 mmol) dissolved in 100 mL of water was added to the red solution under vigorous stirring, followed by the slow addition of concentrated sulphuric acid (42 mL, 17 m, 714 mmol). The hot solution was allowed to cool to room temperature. The 10-molybdo-2-vanadophosphoric acid was then extracted with 500 mL of diethyl ether. Air was passed through the heteropoly etherate (bottom layer) to free it of ether. The solid residue was dissolved in water, concentrated to first crystal formation, as already described, and then allowed to crystallize further. The large red crystals that formed were filtered, washed with water, and air-dried.

Preparation of $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$

Na_2HPO_4 (3.55 g, 25 mmol) was dissolved in 50 mL of water and mixed with (3.05 g, 25 mmol) of sodium metavanadate that had been dissolved by boiling in 50 mL of water. The mixture was cooled and acidified to a red colour with concentrated sulphuric acid (2.5 mL, 17 M, 42.5 mmol). To this mixture was added a solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (66.5 g, 274.8 mmol) dissolved in 100 mL of water. Finally, 42.5 mL of concentrated sulphuric acid was added slowly to the solution under vigorous stirring. With this addition, the dark red colour changed to a lighter red. After cooling the aqueous solution, heteropoly acid was then extracted into 200 mL of diethyl ether. In this extraction, the heteropoly etherate was present as the middle layer; the bottom layer (water) was yellow and probably contained vanadyl species. After separation, a stream of air was passed through the heteropoly etherate layer to free it of ether. The solid orange residue was dissolved in 50 mL of water, concentrated to the first appearance of crystals in a vacuum desiccator over concentrated sulphuric acid, and then allowed to crystallize further. The orange crystals that formed were filtered, washed with water, and air-dried.

General procedures for the oxidation of benzaldehyde using H_2O_2 as the oxidizing agent

Method A (microwave irradiation conditions). Benzaldehyde, heteropolyacid compound and H_2O_2 are mixed thoroughly in a small beaker. The mixture was placed in microwave oven and irradiated for 3 min. at 10–80 % power (full power 1000 watts). Then to the final mixture was added 10 % aqueous solution of NaHCO_3 and the mixture was filtered. The carboxylic acids were precipitated by adding 6 M HCl to the filtrate. The solid product was collected and washed with H_2O . Adding 2,4-dinitrophenylhydrazine (DNP) reagent precipitated the product. The products were characterized by comparison of their spectroscopic data (IR, $^1\text{H-NMR}$ and MS), and melting points with those of authentic samples.

Method B (magnetic stirrer (25 °C) conditions). To a stirred mixture of the aldehyde (2 mmol) and H_2O_2 (3 mmol) was added $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ (0.25 mol %). Then stirring was continued at room temperature under solvent-free conditions. The progress of the reaction was monitored by TLC.

Method C (reflux conditions). The aldehyde (5 mmol) was dissolved in a mixed solvent (10 mL ethanol + 5 mL H_2O). Then heteropolyacid (0.1g, 10^{-2} mmol) was added to the solution. The reaction mixture was refluxed in a 25-mL round-bottom flask equipped with a magnetic stirrer, reflux condenser and thermometer. While the solution was vigorously stirred for 10 min, H_2O_2 (5mL, 165 mmol) was added to the solution. The reaction mixture was stirred and refluxed for 3–10 h at 70 °C.

General procedure for the oxidation of benzyl aldehyde using KMnO_4 as the oxidant

Preparation of oxidant (KMnO_4). The oxidant is prepared by grinding equal amounts of potassium permanganate and copper sulphate pentahydrate in a mortar until homogeneous or

by adding a concentrated aqueous solution of potassium permanganate to alumina, giving a paste that was then ground with an equal amount of copper sulphate pentahydrate. Addition of alumina as a solid support did not improve the yields of these reactions. The best results were obtained when KMnO_4 was first mixed with copper sulphate pentahydrate (or a 20/80 mixture of copper sulphate pentahydrate and alumina) to give a reagent that has previously been extensively used as a heterogeneous oxidant.

General procedure for the oxidation using KMnO_4 as oxidant

All reaction mixtures were refluxed in a 100-mL, two necked round-bottom flask equipped with a magnetic stirrer, reflux condenser, and thermometer. Benzylaldehyde (5 mmol) and a portion of the oxidant (4 g) was added to the mixed solvent (20 mL ethanol + 10 mL H_2O) and 0.5 g $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ (0.025 mol). The reaction mixture was stirred vigorously and refluxed for 4–8 h at 80 °C until TLC analysis indicated completion of the reaction. Then the suspension was cooled and the aqueous layer separated by filtration through a short column of sodium chloride. The water layer was acidified to pH 3 by the addition of hydrochloric acid. The precipitate of benzoic acid was separated by filtration and washed with CH_2Cl_2 or cold water (3×10 mL). If greater purity is required, the product could be recrystallized.

Recycling of the catalyst

At the end of the oxidation of aldehydes to carboxylic acids, the catalyst was filtered and washed with dichloromethane. In order to know whether the catalyst would succumb to poisoning and lose its catalytic activity during the reaction, the reusability of the catalyst was investigated. For this purpose, after completion of the reaction, dichloromethane was added to the reaction mixture. All compounds were soluble in dichloromethane except the catalyst. Thus, it could be separated by simple filtration, washed with dichloromethane, dried at 90 °C for 1 h, and reused in another reaction with the same substrate. Even after five runs for the reaction, the catalytic activity of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ was almost the same as that of freshly used catalyst. The results are summarized in Table I. The IR spectra of the resulting solids indicate that the catalyst can be recovered without structural degradation.

TABLE I. Reuse of the catalyst in the oxidation of 4-chlorobenzaldehyde (isolated yield is based on the weight of the pure product obtained)

Times used	Isolated yield, %
1	95
2	92
3	94
4	91
5	93

RESULTS AND DISCUSSION

The oxidation of aromatic aldehydes by H_2O_2 or KMnO_4 was examined in the presence of a variety of heteropolyacids and transition metal-substituted polyoxometalates. Although it is difficult to explain the different activities of these HPAs, certainly there is a complex relationship between the activity and structure of the polyanion. By changing the constituent elements of the polyanion (both hetero- and addenda-atoms), the acid strength of the HPAs and their catalytic activity can be varied over a wide range.²⁴ When the substrate was liquid, the

mole ratio of sub:ox:cat was 1:3:10⁻³ but when substrate was solid the mole ratio was 1:15:10⁻³ or 1:30:10⁻³, depending on the reaction conditions. They are summarized in Table II. It is noticeable that the time of reaction under microwave irradiation was very short with respect to the analogous reactions.²⁵ The Keggin-type polyoxometalates resulted in more effective reactions in comparison to the Well-Dawson-type polyoxometalates (see later Table IV). However, H₆P₂Mo₁₈O₆₂ was more effective than H₃PW₁₂O₄₀ in the oxidation of aldehydes. This may be due to the difference in the reduction potentials of tungsten and molybdenum.

TABLE II. Oxidation of different aromatic aldehyde using H₂O₂ as oxidant under microwave condition

Entry	Aldehyde aromatic	Power, W	Reaction time, s	Isolated yield, %
1	4-Methylbenzaldehyde	30	100	88
2	4-Cholorobenzaldehyde	300	80	95
3	2,6-Dicholorobenzaldehyde	300	120	92
4	2,4-Dicholorobenzaldehyde	300	130	96
5	3,4-Dicholorobenzaldehyde	350	150	90
6	4-Nitrobenzaldehyde	400	120	97
7	3-Nitrobenzaldehyde	500	130	95
8	3,4-Dinitrobenzaldehyde	500	150	94
9	2,3-Dinitrobenzaldehyde	500	150	90
10	Benzaldehyde	500	150	95

Effect of the aldehyde substituent

The effects of various substituents on the yields of oxidation of a range of aromatic aldehydes were examined using H₅PV₂Mo₁₀O₄₀ as the catalyst. The results are given in Tables II and III. Halogens were chosen as electron-withdrawing groups (Table II, entries 2–5), while methyl was chosen as an electron-donating substituent (Table II, entry 1). The yields were generally very good (>80 %) to excellent (>90 %) with no obvious relationship between the aromatic substituent and yield (compare entries 1 with 10 and 2 with 10). A highlight of the method is the ease by which the product may be isolated *via* simple filtration following removal of the solvent.

TABLE III. Oxidation of aromatic aldehydes using H₂O₂ in presence of different solvents under reflux conditions (isolated yield based on the weight of the pure product obtained)

Entry	Aldehyde	Solvent	Time, h	Isolated yield, %
1	4-Nitrobenzaldehyde	20 ml Ethanol + 10 ml H ₂ O	3	95
		10 ml Ethanol + 20 ml H ₂ O	3	90
		15 ml ethanol + 15 ml H ₂ O	4	91
		30 ml Ethanol	5	85
		30 ml H ₂ O	5	85
		Solvent free	8	65
2	3-Nitrobenzaldehyde	20 ml Ethanol + 10 ml H ₂ O	5	89

TABLE III. Continued

Entry	Aldehyde	Solvent	Time, h	Isolated yield, %
2	3-Nitrobenzaldehyde	10 ml Ethanol + 20 ml H ₂ O	7	82
		15 ml Ethanol + 15 ml H ₂ O	8	80
		30 ml Ethanol	10	75
		30 ml H ₂ O	10	79
		Solvent free	12	52
3	4-Chlorobenzaldehyde	20 ml Ethanol + 10 ml H ₂ O	5	94
		10 ml Ethanol + 20 ml H ₂ O	8	88
		15 ml Ethanol + 15 ml H ₂ O	10	84
		30 ml Ethanol	10	78
		30 ml H ₂ O	8	84
4	Benzaldehyde	Solvent free	12	63
		20 ml Ethanol + 10 ml H ₂ O	6	82
		10 ml Ethanol + 20 ml H ₂ O	8	79
		15 ml Ethanol + 15 ml H ₂ O	10	75
		30 ml Ethanol	10	69
		30 ml H ₂ O	8	75
		Solvent free	12	45

Effect of the catalyst structure

The effect of catalyst structure on the oxidation of aromatic aldehydes is summarized in Table IV. 4-Chlorothiophenol was used as the model compound and the amount of each catalyst was kept constant. In the Keggin-type polyoxometalates series, H₅PV₂Mo₁₀O₄₀ showed the highest catalytic activity. In general, the heteropoly salt type catalysts were less efficient than the heteropolyacids. The Keggin-type polyoxometalates led to a more effective reaction in comparison with the Well–Dawson type polyoxometalates. Thus, H₆P₂Mo₁₈O₆₂ was again more effective than H₆P₂W₁₈O₆₂ in the oxidation of aldehydes, possibly due to the difference in the reduction potentials tungsten and molybdenum. However, the results indicated that the highest yield of products was obtained with H₅PV₂Mo₁₀O₄₀ as catalyst (Table III). This behaviour is found to be quite general. The high activity of H₅PV₂Mo₁₀O₄₀ in comparison of the other HPAs (Table IV) confirmed that in addition to H⁺, the V⁵⁺ probably played a catalytic role in the reaction.

TABLE IV. Oxidation of aldehydes using KMnO₄ as the oxidant in the presence of different heteropolyacids using microwave radiation

Entry	Aldehyde	Catalyst	Reaction time, s	Power, W	Yield, %
1	4-Methylbenzaldehyde	H ₅ PV ₂ Mo ₁₀ O ₄₀	30	100	88
		H ₆ PV ₃ Mo ₉ O ₄₀	40	100	86
		H ₄ PVMo ₁₁ O ₄₀	50	100	82
		H ₃ PMo ₁₂ O ₄₀	60	100	78
		H ₆ P ₂ Mo ₁₈ O ₆₂	80	200	74

TABLE IV. Continued

Entry	Aldehyde	Catalyst	Reaction time, s	Power, W	Yield, %
1	4-Methylbenzaldehyde	H ₃ PW ₁₂ O ₄₀	90	100	70
		H ₆ P ₂ W ₁₈ O ₆₂	140	200	70
		None	300	500	25
2	4-Chlorobenzaldehyde	H ₅ PV ₂ Mo ₁₀ O ₄₀	80	300	95
		H ₆ PV ₃ Mo ₉ O ₄₀	100	280	95
		H ₄ PVMo ₁₁ O ₄₀	110	300	92
		H ₃ PMo ₁₂ O ₄₀	120	500	86
		H ₆ P ₂ Mo ₁₈ O ₆₂	130	600	82
		H ₃ PW ₁₂ O ₄₀	130	500	88
		H ₆ P ₂ W ₁₈ O ₆₂	140	1000	81
		None	320	2000	28
3	4-Nitrobenzaldehyde	H ₅ PV ₂ Mo ₁₀ O ₄₀	120	400	97
		H ₆ PV ₃ Mo ₉ O ₄₀	100	450	97
		H ₄ PVMo ₁₁ O ₄₀	150	600	96
		H ₃ PMo ₁₂ O ₄₀	180	1000	88
		H ₆ P ₂ Mo ₁₈ O ₆₂	180	1000	86
		H ₃ PW ₁₂ O ₄₀	170	800	84
		H ₆ P ₂ W ₁₈ O ₆₂	180	1000	81
		None	480	2000	27
4	3-Nitrobenzaldehyde	H ₅ PV ₂ Mo ₁₀ O ₄₀	130	500	98
		H ₆ PV ₃ Mo ₉ O ₄₀	100	500	98
		H ₄ PVMo ₁₁ O ₄₀	160	600	96
		H ₃ PMo ₁₂ O ₄₀	200	1000	87
		H ₆ P ₂ Mo ₁₈ O ₆₂	280	1000	86
		H ₃ PW ₁₂ O ₄₀	250	1300	84
		H ₆ P ₂ W ₁₈ O ₆₂	300	1300	82
None	540	2500	24		

Effect of microwave irradiation

In recent years, a practical dimension to microwave heating protocols was added by accomplishing reactions on solid supports under solvent-free conditions.²¹ These solvent-free microwave-assisted reactions provide an opportunity to work with open vessels, thus avoiding the risk of high-pressure development and increasing the potential of such reactions to large-scale production. For the first time, results on this environmentally benign microwave approach for the oxidation of aromatic aldehyde in the presence of H₅PV₂Mo₁₀O₄₀ are described herein. The results showed that, 4-chlorobenzaldehyde could easily be oxidized but hydroxybenzaldehydes could not. Other mono-substituted benzaldehydes showed different behaviours (Table IV).

A comparison of the methods

The results also showed that under microwave irradiation, the oxidation readily proceeds over mixed addenda heteropolyacid H₅PV₂Mo₁₀O₄₀ catalysts

loadings under solvent-free conditions in very short times (1–3 min) (Table V). This can be due to the polar nature of the reaction intermediates that couple efficiently with the microwaves and hence, increase the yield and accelerate the rate. Clearly, this method minimizes the longer reaction times required under thermal conditions.

TABLE V. Comparison of the different methods employed

Entry	Aldehyde	Test method	Time	Yield, %
1	4-Methylbenzaldehyde	Reflux (solvent)	4 h	84
		Heated (without solvent)	3.5 h	86
		Magnetic stirrer (25 °C)	10 h	82
		Microwave irradiation	30 s	88
2	4-Chlorobenzaldehyde	Reflux (solvent)	5 h	94
		Heated (without solvent)	5 h	92
		Magnetic stirrer (25 °C)	14 h	90
		Microwave irradiation	80 s	94
3	4-Nitrobenzaldehyde	Reflux (solvent)	3 h	95
		heated (without solvent)	2.5 h	92
		Magnetic stirrer (25 °C)	10 h	96
		Microwave irradiation	120 s	100
4	3-Nitrobenzaldehyde	Reflux (solvent)	5 h	89
		Heated (without solvent)	4.5 h	90
		Magnetic stirrer (25 °C)	12 h	88
		Microwave irradiation	130 s	98
5	Benzaldehyde	Reflux (solvent)	6 h	82
		Heated (without solvent)	7 h	76
		Magnetic stirrer (25 °C)	10 h	74
		Microwave irradiation	150 s	95

Effect of the oxidant

This reaction was carried out using either H₂O₂ or KMnO₄ as the oxidizing agent under mild conditions. The effect of the oxidant on the oxidation of aromatic aldehydes in the presence of H₅PV₂Mo₁₀O₄₀ is presented in Table VI.

TABLE VI. Oxidation of aldehydes by different oxidants in the presence of H₅PV₂Mo₁₀O₄₀

Entry	Aldehyde	Oxidant	Time, h	Yield, %
1	4-Nitrobenzaldehyde	KMnO ₄	5	97
		H ₂ O ₂	3	95
		None	8	20
2	3-Nitrobenzaldehyde	KMnO ₄	5	98
		H ₂ O ₂	5	89
		None	8	17
3	4-Chlorobenzaldehyde	KMnO ₄	7	96
		H ₂ O ₂	5	94
		None	10	18

TABLE VI. Continued

Entry	Aldehyde	Oxidant	Time, h	Yield, %
4	4-Methylbenzaldehyde	KMnO ₄	4	92
		H ₂ O ₂	4	98
		None	8	27
5	Benzaldehyde	KMnO ₄	5	96
		H ₂ O ₂	6	69
		None	8	25
6	2,6-Dichlorobenzaldehyde	KMnO ₄	8	88
		H ₂ O ₂	7	92
		None	10	11
7	2,4-Dichlorobenzaldehyde	KMnO ₄	8	90
		H ₂ O ₂	7	91
		None	10	10
8	3,4-Dichlorobenzaldehyde	KMnO ₄	8	87
		H ₂ O ₂	7	91
		None	10	11
9	3,4-Dinitrobenzaldehyde	KMnO ₄	8	89
		H ₂ O ₂	7	92
		None	10	10

CONCLUSIONS

By changing the constituent elements of the polyanion (both hetero and addenda atoms), the acid strength of HPAs as well as their catalytic activity can be varied over a wide range. For the first time, using the inexpensive and easily prepared H₅PV₂Mo₁₀O₄₀ solid catalyst, oxidation of aromatic aldehydes with electron-withdrawing and electron-donating groups to the corresponding carboxylic acids was studied. The results showed that the catalyst type is important as well as the solvent and temperature, but that the reaction withstands a range of substituents. The Keggin-type polyoxometalates were superior to the Well–Dawson type polyoxometalates.

ИЗВОД

„ЗЕЛЕНИ“, ПОНОВО УПОТРЕБЉИВ, ВИСОКО ЕФИКАСАН ЧВРСТИ КИСЕЛИ КАТАЛИЗАТОР ЗА ОКСИДАЦИЈУ АЛДЕХИДА ДО ОДГОВАРАЈУЋЕ КИСЕЛИНЕ СА H₂O₂ И KMnO₄:H₅PV₂Mo₁₀O₄₀ (10-МОЛИБДО-2-ВАНАДО ФОСФОРНЕ ХЕТЕРОПОЛИ КИСЕЛИНЕ)

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Предмет рада је оксидација ароматичних алдехида до одговарајућих карбоксилних киселина, употребом водоник-пероксида као реагенса, уз H₅PV₂Mo₁₀O₄₀ као катализатора. Наведени систем представља ефикасан, погодан и практичан метод за оксидацију ароматичних алдехида. Полиоксометалати Keggin и Well–Dawson типа су међусобно упоређени у односу на њихову релативну стабилност, тврдоћу и киселост.

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