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ORIGINAL PAPER

Green oxidation of alcohols with hydrogen peroxide catalyzed by a tetra-cobalt polyoxometalate in water

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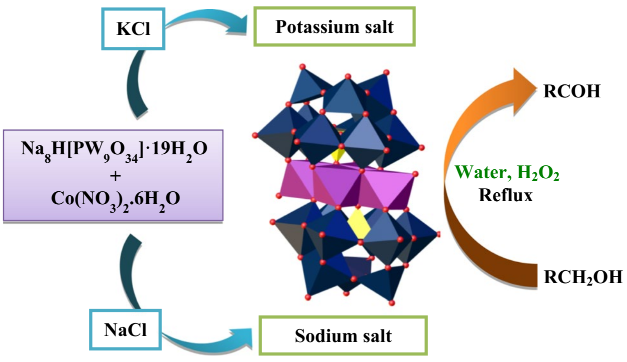
Abstract In this work it was demonstrated that the sodium and potassium salts of a sandwich-type tetra-cobalt tungstophosphate, $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, are efficient catalysts for the selective oxidation of alcohols into corresponding aldehydes with hydrogen peroxide in water. Among these two salts, $Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 27H_2O$ complex showed better catalytic activity for the alcohols' oxidation. Using trace amounts of catalyst, different benzylic and aliphatic hydroxyl groups were converted into the corresponding carbonyl compounds in high to excellent yields.

Graphical Abstract In this work green and efficient catalytic oxidation of various alcohols to aldehydes and ketons with a sandwich-type tetra-cobalt tungstophosphate, $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, is developed. High-to-excellent yields for oxidation of different alcohols by hydrogen peroxide in water are some advantageous of this catalytic system.



Keywords Sandwich-type polyoxometalate · Catalysis · Oxidation · Alcohol · Hydrogen peroxide · Water

Introduction

Selective oxidation of alcohols to their corresponding carbonyl compounds is one of the most important methods in organic synthesis processes and is widely used in perfumery and pharmaceutical industries [1–3]. Increasing environmental concerns necessitate the development of ecofriendly techniques for alcohol oxidation transformations [4]. Therefore, it is favorable to develop alternative processes with new catalysts for the conversion of different alcohols into corresponding aldehydes and ketones [5]. In this manner, the design of new synthesis methods that bring "greenness" into the aldehyde and ketone production is of high importance. Thus, (1) utilizing green oxidants (H_2O_2 is desirable from the stand point of green sustainable chemistry because water is the only waste for hydrogen peroxide), (2) employing clean solvents (particularly aqueous media), and (3) designing environmentally favorable catalysts with high activity and selectivity are important for this purpose [6–11]. Therefore, employing of water as solvent and H_2O_2 as a green oxidant are of great interest in green chemistry.

The diversity, availability, and low toxicity of polyoxometaslates (POMs) have led to many recent applications of these compounds in catalysis, medicine, and materials science [12–15]. In POMs the d^0 electronic configuration renders them oxidatively resistant and, therefore, exclusively attractive as heterogeneous and homogeneous oxidation catalysts [16, 17]. $[PW_{11}O_{39}]^{7-}$ [18], $[NaP_5W_{30}O_{110}]^{14-}$ [19], $H_5[PV_2Mo_{10}O_{40}]$ [20], $[IMo_6O_{24}]^{5-}$ [21], and $Na_{6.3}Fe_{0\cdot 9}[AlMo_{11}O_{39}]\cdot 2H_2O$ [22] are some of the reported

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POM catalysts for the alcohol oxidation. In all of these works, despite the high-to-excellent yields of carbonyl compounds, environmentally undesirable solvents were used. In the class of transition-metal-substituted POMs, the sandwich-type compounds represent the largest subclass [23]. These compounds are a versatile and robust group of POMs with applications in catalysis. For example, it was shown that $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$ has a good catalytic activity for alcohol oxidation in water [24]. Also, different sandwich-type POMs such as $H_2Na_{14}[Fe^{III}_2(NaOH_2)_2(P_2W_{15}O_{56})_2]$, $[(Mn^{II}(H_2O)_3)_2(WO_2)_2(BiW_9O_{33})_2]^{10-}$ and $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ have been used in epoxidation of alkenes [25–27]. For the first time, the synthesis of $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (Co-STPOM) as a sandwich-type polyoxoanion has been reported by Weakley et al. [28]. This sandwich-type POM has gained significant interest as catalyst for water oxidation [29–33]. However, the catalytic properties of this compound in the oxidation of organic substrates really lagged behind.

In continuation of our ongoing researches on the development of novel methods for oxidation of organic compounds in the presence of sandwich-type POMs [34], herein a simple and efficient method for oxidation of alcohols catalyzed by different salts of Co-STPOM has been reported. These catalytic reactions took place "in water", and 30 % hydrogen peroxide was used as oxidant. Also, a comparison between catalytic activity of sodium and potassium salts of Co-STPOM (K-Co-STPOM and Na-Co-STPOM) in the oxidation of benzyl alcohol was achieved.

Experimental

Reagents and methods

All chemicals were of analytical grade, commercially available, and used without further purification unless otherwise stated. Infrared spectra (KBr pellets) were recorded on a JASCO, FT/IR-6300 instrument. The elemental analyses for Co, W and P were performed on a Perkin-Elmer 7300 DV elemental analyzer. The analyses of oxidation products were quantitatively carried out by gas chromatography (GC) on a Shimadzu GC-16A instrument using a 2-m column packed with silicon DC-200 and FID detector.

Preparation of the Co-STPOM

Solid B-$Na_8H[PW_9O_{34}]\cdot 19H_2O$ (4.00 g, 1.4 mmol, 2 equiv) was dissolved in 20 mL water. With stirring at ambient temperature, $Co(NO_3)_2\cdot 6H_2O$ (0.82 g, 2.8 mmol, 4 equiv) was added to this solution. The resulting purple suspension was heated to 60 °C for 20 min until a deep purple solution was resulted. To this hot reaction mixture solid NaCl (2.4 g) as well as 2 mL EtOH was added and the solution was heated to 80 °C for 1 h. A purple to violet crystalline solid precipitated upon cooling to room temperature overnight. The solid was collected by filtration, washed three times with 1 mL of ice cold water, and recrystallized from a minimum amount of hot water (70 °C) with cooling to room temperature overnight. After filtration and drying in vacuo, $Na_{10}[Co_4(PW_9O_{34})_2]$ was isolated as purple violet crystals (1.914 g, 48 % based on Co). The basic structure and purity of the compound were confirmed by FT-IR and elemental analysis [25, 28 and 35].

Typical procedure for catalytic oxidation of alcohols

The catalytic reactions were carried out in a 10-mL round-bottom flask equipped with a magnetic stirring bar and a reflux condenser. The Co-STPOM catalyst (0.001 mmol), water (3 mL), alcohol (1 mmol), and H_2O_2 (9.8 mmol) were charged in the reaction vessel. The reaction was carried out at reflux and progress of the reaction was detected by TLC and GC. After completion of the reaction, organic product was isolated by ethyl acetate (3 × 2 mL) and the organic layer was analyzed by gas chromatography or ^1H NMR. Products were assigned by comparing experimental data with authentic samples.

Results and discussion

As mentioned above, the sodium, potassium, and tetra-*n*-butylammonium (TBA-Co-STPOM) salts of Co-STPOM were synthesized according to the published procedures and their synthesis confirmed by elemental analysis and infrared spectroscopy. The IR spectra of these three Co-POM salts are shown in Fig. 1.

All of these compounds showed four characteristic IR bands between 1,100 and 400 cm^{-1} for the Co-STPOM structure [28, 35]. The characteristic IR bands established that Co-STPOM structure has not been changed by different counter ions (TBA, K and Na) (Fig. 2). Also, elemental analysis for all of them showed that the molar ratio for Co:P:W is 2:1:9, respectively, and did not varied when counter ions differed.

Initially the oxidation of benzyl alcohol was selected as a model reaction, and the oxidation of benzyl alcohol in the presence of sodium, potassium, and TBA salts of Co-STPOM with hydrogen peroxide was carried out in water at reflux conditions. In this catalytic system water was used as solvent because it is much cheaper and greener than all of the other organic solvents. At the end of reaction, the organic products were isolated from the aqueous phase by simple extraction using ethyl acetate (3 × 2 mL).

After 2 h of oxidation reaction, the sodium salt of Co-STPOM showed very high catalytic activity (98 % yield

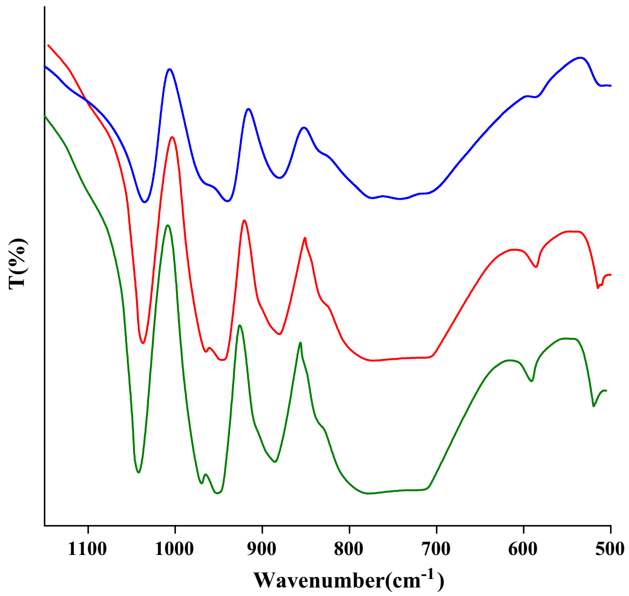


Fig. 1 Infrared spectra of Na-Co-STPOM (*blue*), K-Co-STPOM (*red*), and TBA-Co-STPOM (*green*)

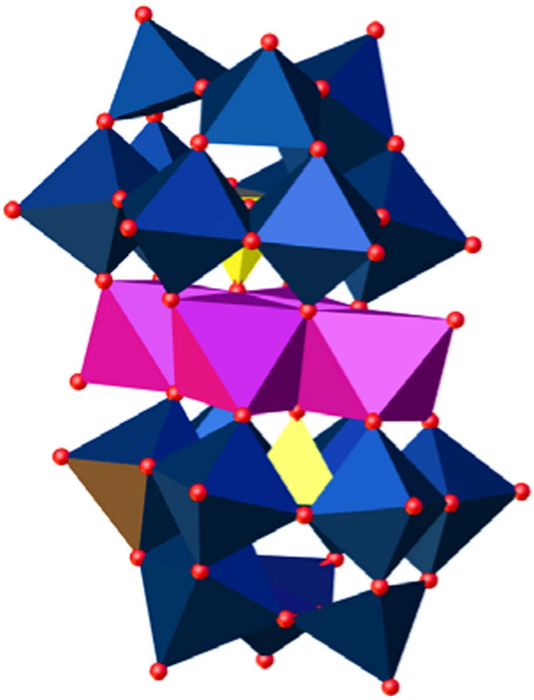


Fig. 2 Polyhedral representation of the Co-STPOM structure

for benzaldehyde), whereas potassium salt of this POM showed moderate activity (75 % yield) for oxidation of benzyl alcohol by hydrogen peroxide in water. It was very interesting that the TBA salt of Co-STPOM showed very low catalytic activity (only 17 % yield). These observations demonstrated that the catalytic activity of Co-STPOM improved with the increasing solubility of the catalyst. Compared to potassium salt, sodium salt has better solubility in water; thus, a better activity for Na-Co-STPOM could be seen in the conversion curves for these three POM catalysts (Fig. 3).

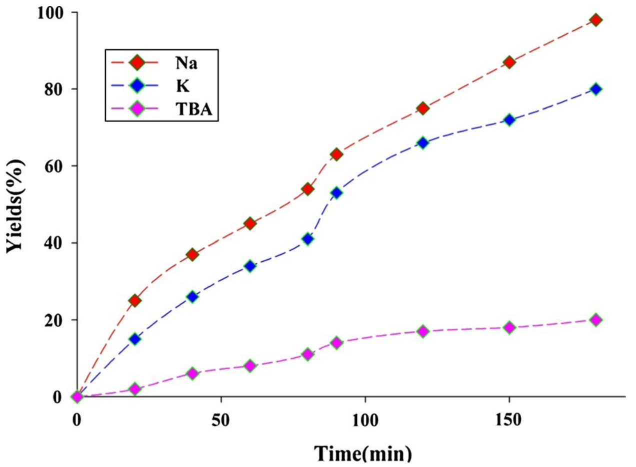


Fig. 3 The conversion-time curves for oxidation of benzyl alcohol with Na, K, and TBA salts of Co-STPOM. Reaction conditions: benzyl alcohol (1 mmol), catalyst (0.001 mmol), water (3 mL), 30 % H_2O_2 (9.8 mmol) at reflux

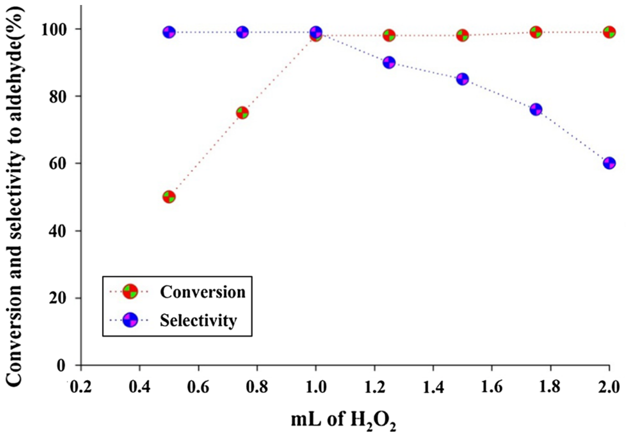


Fig. 4 The effect of hydrogen peroxide amounts in the oxidation of benzyl alcohol with Na-Co-STPOM. Reaction conditions: benzyl alcohol (1 mmol), catalyst (0.001 mmol), water (3 mL), various amounts of 30 % H_2O_2 at reflux

According to these results, Na-Co-STPOM was selected as the best catalyst for the oxidation of different alcohols. In order to optimize the other reaction conditions, an attempt was made to investigate the effects of oxidant quantities on the oxidation of benzyl alcohol. The oxidation reaction was performed by different molar ratios of oxidant to benzyl alcohol as model substrate. The catalytic oxidation by 9.8 equiv of H_2O_2 afforded 98 % benzaldehyde in the presence of Na-Co-POM. Higher amounts of H_2O_2, greater than 9.8 equiv, led to a growth in the reaction rate but decreased aldehyde yield and increased the corresponding carboxylic acid (Fig. 4). The reasonable high conversion efficiency along with excellent selectivity in aldehyde formation was obtained by 9.8 equiv of H_2O_2.

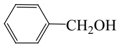
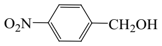
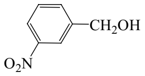
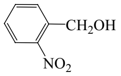
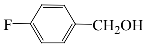
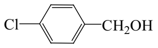
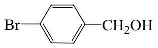
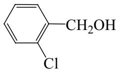
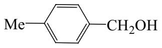
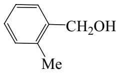
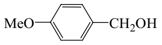
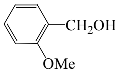
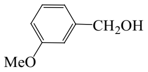
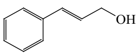
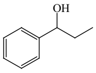
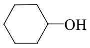
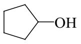
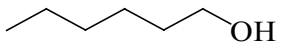
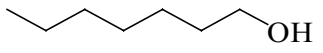
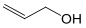
After optimizing the reaction conditions, the performance of this catalytic system in the oxidation of various alcohols was investigated by a molar ratio of 1:1,000:9,800 for catalyst:substrate:oxidant. Results for the oxidation of different primary and secondary alcohols into the corresponding carbonyl compounds at optimal reaction conditions are summarized in Table 1.

The electronic nature and the position of the substituent showed little effect on the reaction process. Both electron-withdrawing and electron-donating substituents, such as NO_2, F, Cl, Br, OMe, and Me on the benzene ring gave the desired products (Table 1, entries 1–15). Different alcohols with electron-donating substituent converted to the corresponding aldehydes even faster than benzyl alcohol. For example, oxidation of 4-methyl benzyl alcohol or 4-methoxy benzyl alcohol gave 97 % 4-methyl benzaldehyde or 99 % 4-methoxy benzaldehyde, respectively (Table 1, entries 9 and 11). Similarly 2-methoxy, 3-methoxy, and 2-methy benzyl alcohols are oxidized by 97–99 % yields (Table 1 entries 10, 12, and 13), which shows for the electron donating groups the substituent positions has no particular effect in the reaction. Benzyl alcohols with electron-withdrawing substituent were also converted into the corresponding aldehydes in relatively high yields (Table 1, entries 2–5). The results also showed that the oxidation of linear aliphatic alcohols (for example 1-octanol and 1-heptanol) is much more difficult than that for benzylic and cyclic alcohols (Table 1, entries 16–19). For cinnamyl alcohol and 1-propenol, the corresponding aldehydes were produced without oxidation of C=C double bond (Table 1, entries 14 and 20). The oxidation of benzyl alcohol was also performed in the presence of higher amounts of catalyst and hydrogen peroxide. Results showed that excessive amounts of H_2O_2 (about 4 mL) and catalyst (about 0.01 mmol) are needed for complete conversion of benzyl alcohol into benzoic acid at appropriate time.

The study of catalyst recyclability and stability in any catalytic process is very important. It is reported that transition-metal-substituted “sandwich type” POMs compared with Keggin type POMs, $[PW_{12}O_{40}]^{3-}$ and $[PW_{11}O_{39}]^{7-}$, are more stable catalysts in the presence of aqueous hydrogen peroxide [36]. Also, in the other studies, various iron-containing POMs have been investigated and results showed that these compounds are hydrolytically stable and have good activities for alkene oxidation [25, 37–43].

In this regard, the recovery, reusability, and stability of the Na-Co-STPOM catalyst were also investigated at the end of reaction. To evaluate the reusability and stability of the catalyst, the recyclability of catalyst in the benzyl alcohol oxidation was studied. After completion of the reaction, the organic products were extracted from the aqueous phase by ethyl acetate as a safe solvent and the aqueous solution of catalyst was reused directly for the next round of reaction without further purification. At the subsequent oxidation reaction, re-addition of benzyl alcohol and H_2O_2 to the aqueous solution of the catalyst was sufficient. The catalytic activity of Na-Co-STPOM in oxidation of benzyl alcohol for five catalytic cycles is shown in Table 2. Results indicated that Na-Co-STPOM catalyst could be

Table 1 Selective oxidation of different alcohols to the corresponding aldehyde using Na-Co-POM

Entry	Substrate	Time (h)	Yields (%)^b
1		3	97
2		4	95
3		4.15	95
4		4.30	95
5		6	98
6		6.15	97
7		6.45	98
8		6.15	92
9		2	97
10		2.10	97
11		2	99
12		2.05	99
13		2.30	99
14		4	97
15		3	96
16		4	85
17		4	80
18		5	83
19		5	81
20		3.5	98

Reaction conditions: alcohol (1 mmol), catalyst (1 μmol), water (3 mL), 30 % H_2O_2 (9.8 mmol) at Reflux

[a] Yields refer to GC yields

Table 2 Recycling data for Na-Co-STPOM as catalyst in the oxidation of benzyl alcohol

Run	Yields (%)[a]
1	97
2	94
3	92
4	85
5	80

Reaction conditions: benzyl alcohol (1 mmol), catalyst (0.001 mmol), Water (3 mL), 30 % H_2O_2 (9.8 mmol) at reflux in 3 h reaction

[a] Yields refer to GC yields

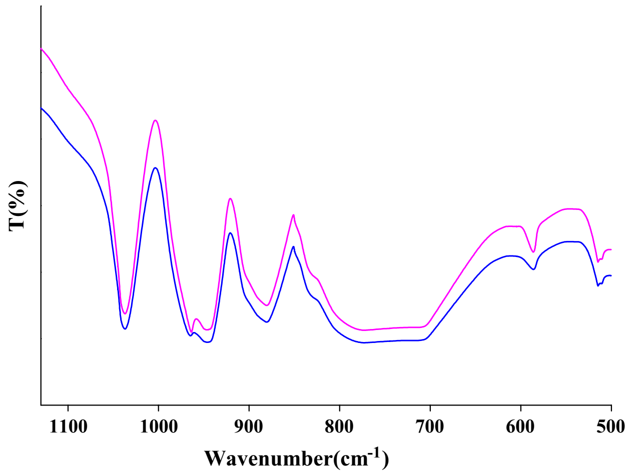


Fig. 5 FTIR spectra of recovered Na-Co-STPOM after run1 (*blue*) and 5 (*pink*)

efficiently recovered and recycled for three times and after that decrease in the catalytic activity was observed.

Also, the IR spectra of the recycled catalyst for cycles 1 and 5 were very similar (Fig. 5). In these two spectra, characteristic IR bands for the structure have not changed. This observation confirmed that the structure of recycled catalyst is preserved and is stable at least for two run oxidation reaction. Results were also confirmed by the previous reports [37, 43, 44].

Conclusion

In summary, a new active and recyclable catalyst, Na-Co-STPOM, for the oxidation of alcohols with hydrogen peroxide in water has been reported. Compared to potassium and TBA salts, Na-Co-STPOM showed a better activity for alcohol oxidation in water. The oxidation of primary and secondary alcohols was also performed in the presence of above-mentioned catalyst. Na-Co-STPOM was recycled several times without any obvious loss in activity. So, this catalytic system is ecofriendly and a practical system for alcohol oxidation.

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