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Oxidation of 1-propanol to propionic acid with hydrogen peroxide catalysed by heteropolyoxometalates

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Abstract

Background: Propionic acid as a very valuable chemical is in high demand, and it is industrially produced via the oxo-synthesis of ethylene or ethyl alcohol and via the oxidation of propionaldehyde with oxygen. It is urgent to discover a new preparation method for propionic acid via a green route. Recyclable amino-acid-based organic–inorganic heteropolyoxometalates were first used to high-efficiently catalyse the selective oxidation of 1-propanol to propionic acid with H_2O_2 as an oxidant.

Result: A series of amino-acid-based heteropoly catalysts using different types of amino acids and heteropoly acids were synthesized, and the experimental results showed proline-based heteropolyphosphatotungstate $(ProH)_3[PW_{12}O_{40}]$ exhibited excellent catalytic activity for the selective catalytic oxidation of 1-propanol to propionic acid owing to its high capacity as an oxygen transfer agent and suitable acidity. Under optimized reaction conditions, the conversion of 1-propanol and the selectivity of propionic acid reached 88% and 75%, respectively. Over four cycles, the conversion remained at >80%, and the selectivity was >60%. $(ProH)_3[PW_{12}O_{40}]$ was also used to catalyse the oxidations of 1-butanol, 1-pentanol, 1-hexanol, and benzyl alcohol. All the reactions had high conversions, with the corresponding acids being the primary oxidation product.

Conclusions: Proline-based heteropolyoxometalate $(ProH)_3[PW_{12}O_{40}]$ has been successfully used to catalyse the selective oxidation of primary alcohols to the corresponding carboxylic acids with H_2O_2 as the oxidant. The new developed catalytic oxidation system is mild, high-efficient, and reliable. This study provides a potential green route for the preparation propionic acid.

Keywords: Selective oxidation, Amino acid, Heteropolyoxometalate, 1-Propanol, Propionic acid

Introduction

Propionic acid, a very valuable chemical, is widely used as a preservative in the feed, food, and pharmaceutical industries and incorporated in the perfume, herbicide, and polymer industries [1, 2]. Propionic acid is industrially produced via the oxo-synthesis of ethylene or ethyl alcohol and via the oxidation of propionaldehyde with oxygen [3, 4]. However, these oxidation reactions require the use of an oil-soluble salt or a metal complex as a catalyst under harsh reaction conditions. Therefore, the development of a mild and effective synthetic method for propionic acid is of great significance.

The oxidation of primary alcohols to the corresponding carboxylic acids is one of the most important transformations in organic chemistry [5–9]. Traditionally, 1-propanol can be oxidised to propionic acid by using inorganic oxidants, such as chromate and potassium

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permanganate, which are expensive and generate a large amount of hazardous waste. An alternative route to the oxidation of 1-propanol using environment-friendly and cheap oxidants is preferable. Hydrogen peroxide (H_2O_2) has received considerable attention as a green oxidant over the past several decades owing to its easy availability, mild oxidation conditions, and single by-product (water) [10–13].

Due to their high capacity as oxygen transfer agents [14, 15], polyoxometalates are characterised as efficient catalysts in oxidation reactions with O_2 or H_2O_2 [16–19]. There have been some reports on the oxidation of primary alcohols using heteropolyoxometalates as catalysts [20–23]. Nonetheless, these catalysts only promote the oxidation of primary alcohols to the corresponding aldehydes. Furthermore, most related studies have involved the oxidation of benzyl alcohol as the model substrate and benzaldehyde as the primary product [24, 25]. The selective oxidation of 1-propanol to the corresponding propionic acid via a green route has not been reported in the literature.

In this paper, we present a highly selective oxidation of 1-propanol to propionic acid with high conversion, using a recyclable organic–inorganic heteropolyoxometalate as the catalyst and H_2O_2 as the oxidant. Inexpensive and readily available amino acid is selected as the cation [26–28]. Moreover, its weak acidity can provide a suitable catalytic environment. Amino-acid-based heteropolyoxometalates exhibit good amphiphilicity, which enhances reactivity and realises the separation and recycling of the catalyst. Among the prepared catalysts, proline-based heteropolyphosphatotungstate $(ProH)_3[PW_{12}O_{40}]$ exhibits the best catalytic activity with good recycling efficiency. The study provides a potential green route for the preparation propionic acid.

Materials and methods

Chemicals

L-Proline (Pro), L-aspartic acid (Asp), L-glutamic acid (Glu), and phosphotungstic acid were purchased from Shanghai McLean Biochemical Technology Co., Ltd. Phosphomolybdic acid, silicotungstic acid, ethyl acetate, anhydrous magnesium sulfate, and 30 wt% H_2O_2 were purchased from Sinopharm Chemical Reagent Co., LTD. 1-Propanol and other chemicals were acquired from Shanghai Biological Technology Co., Ltd.

Preparation of catalysts

The synthesis of a proline-based catalyst, $(ProH)_3[PW_{12}O_{40}]$, was chosen as an example. A total of 0.015 mol L-proline and 10 mL of deionised water were added to a 50-mL one-neck flask. The temperature was increased to 60 °C in a water bath; 0.05 mol of phosphotungstic acid was slowly dropped into 10 mL of an aqueous solution while stirring. The mixture was reacted at 60 °C for 24 h. After the reaction, water was removed by rotary evaporation, and the residue was further dried in a blast drying oven to obtain a white solid catalyst $(ProH)_3[PW_{12}O_{40}]$. The synthetic method for other catalysts was similar to that of $(ProH)_3[PW_{12}O_{40}]$.

Catalytic tests

The reaction was carried out in a 25-mL three-neck flask fitted with a reflux condenser tube. Then, 10 mmol of 1-propanol and an appropriate amount of catalyst were added to the flask. The mixture was stirred for 10 min in a 60 °C water bath, and 30 mmol of 30 wt% H_2O_2 solution was slowly added; the reaction was continued for 6 h at 60 °C. After the reaction, the catalyst was separated by centrifugation and reused after drying. The reaction solution was extracted three times with ethyl acetate, and the upper organic phase was combined for qualitative and quantitative analysis by a gas chromatograph with an FID detector. The lower water phase was titrated with 0.05 M NaOH solution for an integrated quantitative analysis of propionic acid.

Results and discussion

Catalyst Characterization

The infrared spectra of L-proline, $H_3PW_{12}O_{40}$, and $(ProH)_3[PW_{12}O_{40}]$ are shown in Fig. 1. The infrared spectrum of $H_3PW_{12}O_{40}$ shows characteristic peaks at 1082 cm^{-1}, 988 cm^{-1}, 896 cm^{-1}, and 805 cm^{-1}, attributable to the stretching vibrations of P-O_a, W = O_d, W-O_b-W, and W-O_c-W, respectively, characteristics of the typical Keggin structure of heteropoly acid [29]. The primary absorption bands of

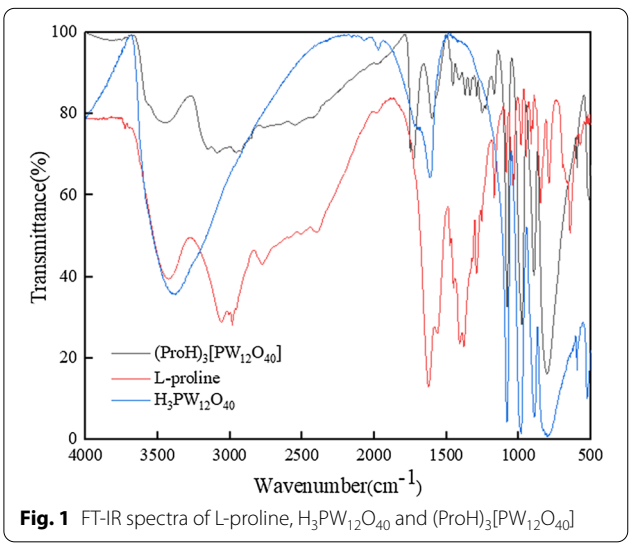


Fig. 1 FT-IR spectra of L-proline, $H_3PW_{12}O_{40}$ and $(ProH)_3[PW_{12}O_{40}]$

$(ProH)_3[PW_{12}O_{40}]$ suggest that the Keggin structure of the heteropoly anion was retained. In the infrared spectrum of L-proline, characteristic absorption peaks at 3400 cm^{-1}, 3050 cm^{-1}, and 1628 cm^{-1} were assigned to the stretching vibrations of -OH, $-NH_2^+$, and C=O, respectively [30, 31]. $(ProH)_3[PW_{12}O_{40}]$ shows a similar pattern of IR peaks; however, compared with L-proline, the $(ProH)_3[PW_{12}O_{40}]$ absorption peaks move slightly towards high wave numbers, indicating the successful synthesis of L-proline-based heteropolyoxometalate $(ProH)_3[PW_{12}O_{40}]$.

Figure 2 shows the ^1H NMR spectra of L-proline and $(ProH)_3[PW_{12}O_{40}]$ using deuterated water and deuterated DMSO as the solvents, respectively. In the ^1H NMR spectrum of L-proline the typical absorption peaks of hydrogen on the ring skeleton was: δ = 1.85–1.93 (m, 2H, CH_2), 1.95–2.22 (m, unequal 2H, CH_2), 3.15–3.25 (m, 2H, CH_2), and 3.95 (t, J = 7.1 Hz, 1H, CH). In contrast to L-proline, the absorption peaks of $(ProH)_3[PW_{12}O_{40}]$ had the same shape, but moved toward the lower field, indicating that L-proline was successfully protonated by phosphotungstic acid. The broad peak between 3–4 ppm indicates the presence of crystalline water.

The XRD pattern of $(ProH)_3[PW_{12}O_{40}]$ (Fig. 3) shows obvious diffraction peaks at 2θ of 7.8°, 9.7°, 18.3°, 29.1°, 32.5°, and 37.8°, which can reflect the characteristic absorption peaks of Keggin structure [22]. However, the diffraction peaks are not exactly the same as those of $H_3PW_{12}O_{40}$, because the hydrogen proton of $H_3PW_{12}O_{40}$ is replaced by the proline cation.

The thermostability of the $(ProH)_3[PW_{12}O_{40}]$ catalyst was studied using a thermogravimetric (TG) test. The TG curve of $(ProH)_3[PW_{12}O_{40}]$ exhibits the stepwise decomposition of proline-based cations and heteropoly anions (Fig. 4). The first decomposition peak appears above 270 °C, suggesting that the catalyst has very high thermostability.

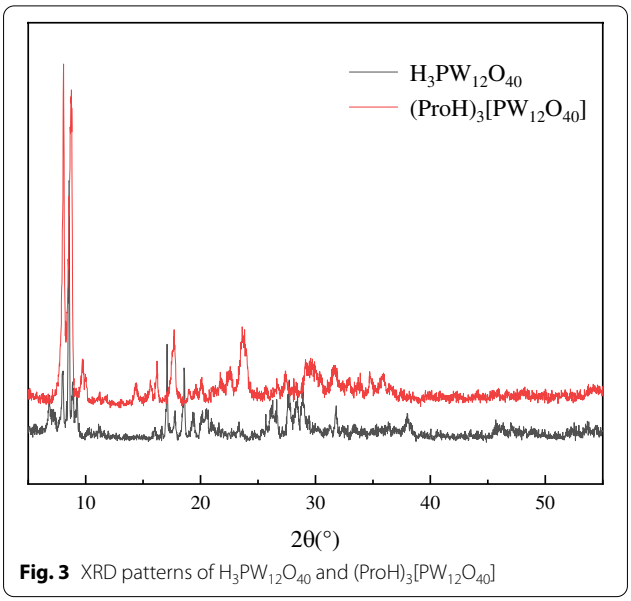


Fig. 3 XRD patterns of $H_3PW_{12}O_{40}$ and $(ProH)_3[PW_{12}O_{40}]$

Catalytic activity of different catalysts

From entry 1 in Table 1, only a small amount of 1-propanol is oxidized by H_2O_2 in the absence of catalyst, and the main oxidation product is propionaldehyde. Herein we synthesised a series of amino-acid-based heteropoly catalysts using different types of amino acids and heteropoly acids to identify the best selective catalysts for the oxidation of 1-propanol to propionic acid. The activities of these catalysts for the selective oxidation of 1-propanol

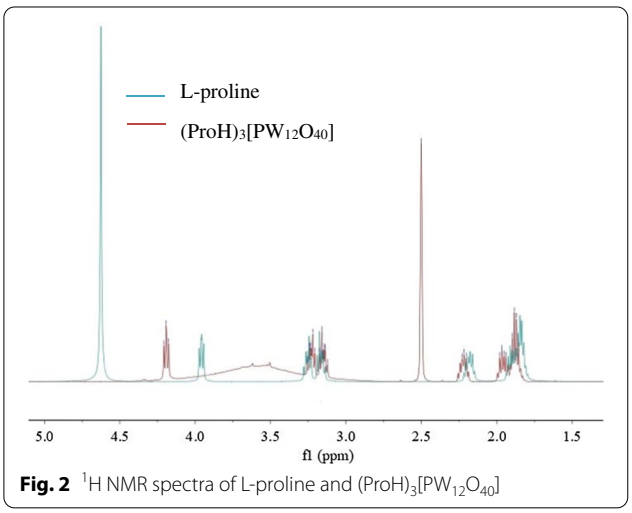


Fig. 2 ^1H NMR spectra of L-proline and $(ProH)_3[PW_{12}O_{40}]$

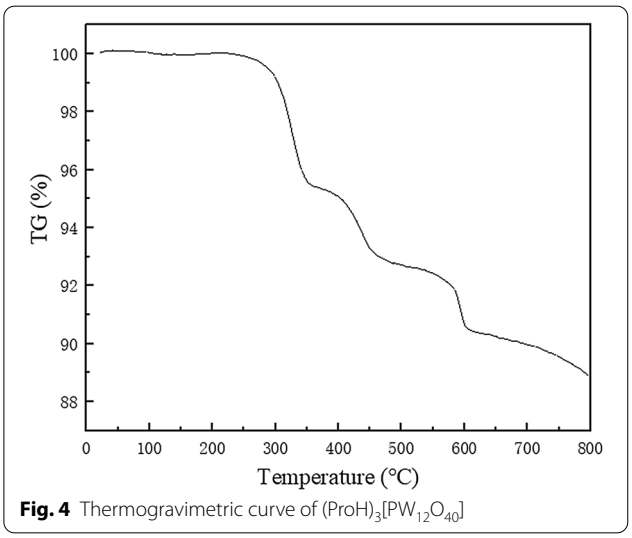


Fig. 4 Thermogravimetric curve of $(ProH)_3[PW_{12}O_{40}]$

Table 1 Catalytic performance of different catalysts[a]

Entry	Catalyst	Acid Strength / mV [b]	Redox potential /V [c]	Conversion /%	Yield/%	Selectivity/%			
						Propionic acid	Propion-aldehyde	Propyl propionate	Others
1	–	–	–	9.36	3.87	41.35	52.56	–	6.09
2	$(ProH)_4[SiW_{12}O_{40}]$	446	0.06	41.71	13.68	32.80	47.85	10.91	8.44
3	$(ProH)_3[PMo_{12}O_{40}]$	427	0.11	30.82	18.31	59.41	29.88	6.72	3.99
4	$(ProH)_3[PW_{12}O_{40}]$	474	0.24	73.98	45.50	61.50	32.51	4.08	1.91
5	$(ProH)_2[HPW_{12}O_{40}]$	595	0.18	65.67	41.94	63.91	25.13	7.74	3.28
6	$(ProH)[H_2PW_{12}O_{40}]$	653	0.13	57.94	27.19	46.93	31.48	17.24	4.35
7	$(AspH)_3[PW_{12}O_{40}]$	490	0.19	69.99	40.53	57.91	25.29	6.97	9.83
8	$(GluH)_3[PW_{12}O_{40}]$	574	0.15	63.54	35.71	56.20	34.56	7.69	1.54
9	$H_3PW_{12}O_{40}$	732	0.13	64.53	36.05	55.87	28.17	13.23	2.73

[a] reaction conditions: n(1-propanol) = 10 mmol, n(catalyst) = 0.1 mmol, n(30%H_2O_2) = 30 mmol, T = 60 °C, t = 6 h, solvent free; [b]0.2 mmol, 25 mL acetonitrile; [c]oxidation potential Vs Ag/AgCl

were fully investigated; the results are listed in Table 1. The acid strength of the catalysts was determined by 1-butylamine titration [32], and the oxidisability of the catalyst was assessed by a redox potential assay. From entries 2–4, the conversion of 1-propanol and the selectivity for propionic acid increased with increasing oxidisability of the catalyst. The catalyst with lower oxidisability primarily catalyses the H_2O_2 oxidation of 1-propanol to propionaldehyde. The acidity of the catalyst also greatly affects the catalytic activity (Table 1), and suitable acidity is required for obtaining propionic acid. Excessive acidity of the catalyst may promote esterification to obtain propyl propionate (Entries 4–6 and 9). Among the different amino-acid-based catalysts tested (entries 4, 7, and 8), the proline-based catalyst $(ProH)_3[PW_{12}O_{40}]$ exhibited the best catalytic activity. In summary, the catalyst with higher oxidation properties and suitable acidity is more suitable for use in the oxidation of 1-propanol to propionic acid.

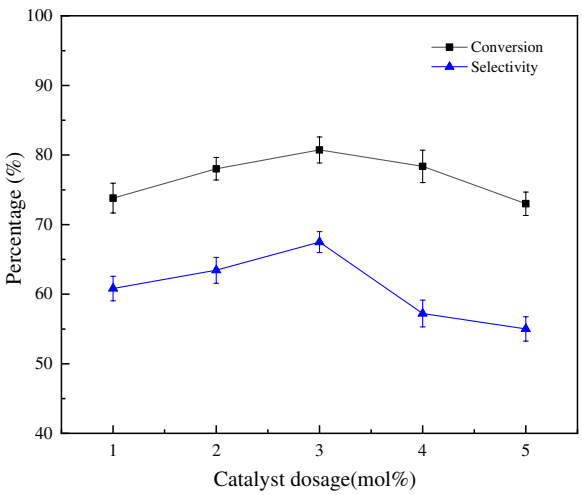


Fig. 5 Influence of catalyst dosage on reaction (n(1-propanol) = 10 mmol, n(H_2O_2) = 30 mmol, T = 60 °C, t = 6 h)

Optimization of catalytic conditions

For the selective oxidation of 1-propanol catalysed by $(ProH)_3[PW_{12}O_{40}]$, various reaction conditions were screened to obtain the optimised conditions that gave propionic acid in greater yields.

Increased catalyst dosage is shown to increase the conversion and selectivity of propionic acid; this effect is limited to catalyst dosages of up to 3 mol% (Fig. 5). When the catalyst dosage was further increased, both the conversion and selectivity of propionic acid decreased, possibly because too much catalyst also improves the decomposition of hydrogen peroxide. Therefore, the best catalyst dosage was 3 mol%.

The oxidant dosage has a significant effect on the reaction. Figure 6 shows that propionic acid yield increases with increasing amount of hydrogen peroxide and reaches a maximum when the molar ratio of H_2O_2 to 1-propanol is 3:1. Additional aqueous H_2O_2 dilutes the concentration of the substrate and the catalyst, resulting in low conversion and selectivity of propionic acid.

The influence of temperature on the reaction is shown in Fig. 7. The conversion and selectivity of propionic acid increased as the reaction temperature was increased from 40 from 60 °C. Nevertheless, a decrease trend for conversion and selectivity is found after 60 °C due to the decomposition of H_2O_2 at higher temperatures, resulting in low yields of propionic acid.

Figure 8 shows the kinetic curves of the reaction at different reaction times. The conversion and selectivity of propionic acid increased significantly upon prolonged the reaction time from 2 to 8 h. After 8 h,

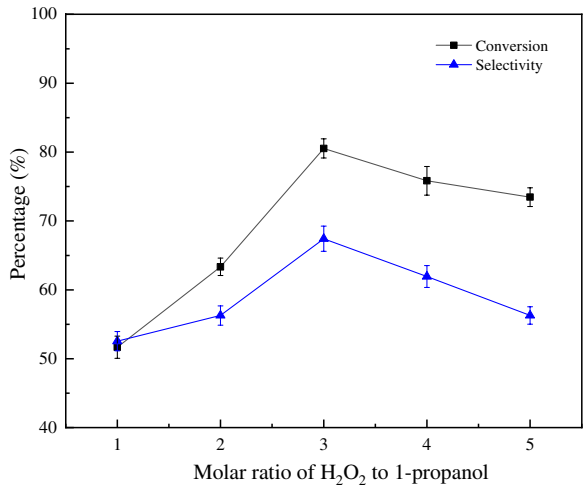


Fig. 6 Influence of oxidant dosage on reaction (n(1-propanol) = 10 mmol, n(catalyst) = 0.3 mmol, T = 60 °C, t = 6 h)

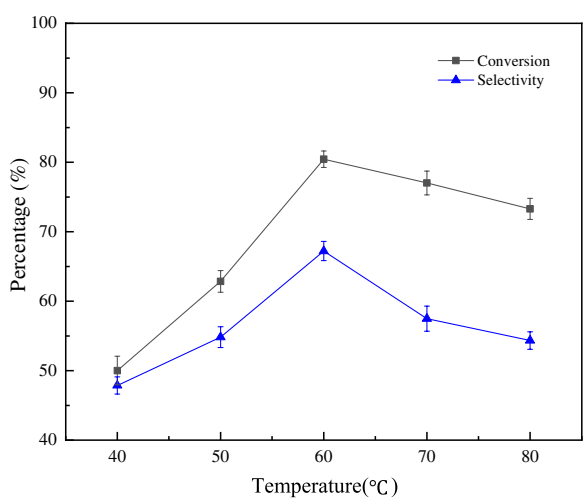


Fig. 7 Influence of temperature on reaction (n(1-propanol) = 10 mmol, n(H_2O_2) = 30 mmol, n(catalyst) = 0.3 mmol, t = 6 h)

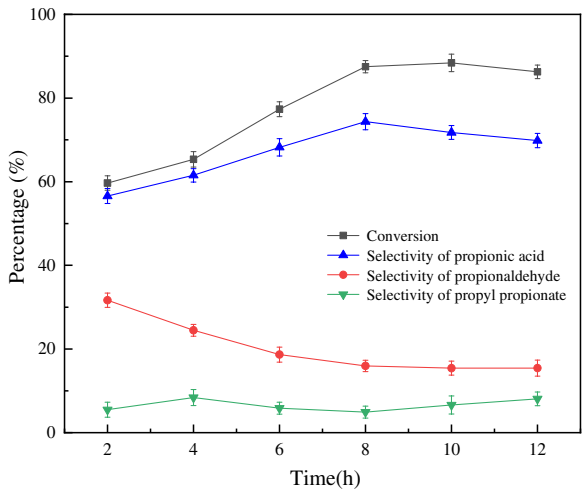


Fig. 8 Influence of time on reaction (n(1-propanol) = 10 mmol, n(H_2O_2) = 30 mmol, n(catalyst) = 0.3 mmol, T = 60 °C)

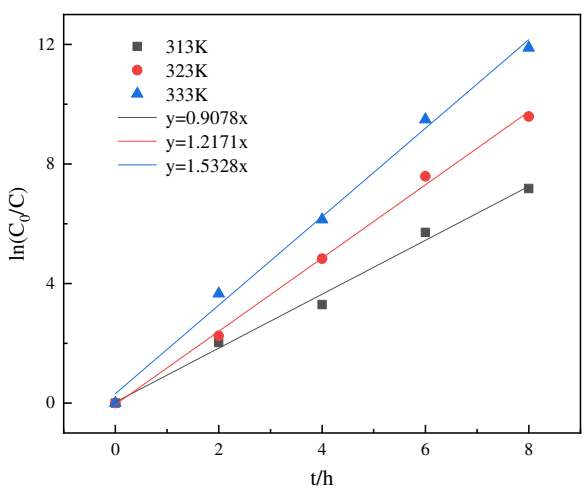


Fig. 9 Reaction rate constants at different temperatures

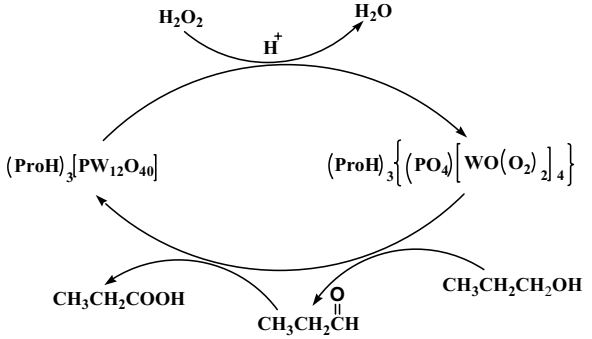
the conversion of 1-propanol remained basically unchanged, and the selectivity of propionic acid began to decrease slightly, because the long reaction time facilitates the esterification of the formed propionic acid with 1-propanol and increases the by-product propyl propionate.

Since the amount of oxidant is excessive, the reaction rate is supposed to only be decided by the concentration of 1-propanol. Reaction rate constants at different temperatures were shown in Fig. 9. According to Arrhenius equation [33], the calculated apparent activation energy is 22.64 kJ/mol.

In summary, the optimum reaction conditions for the preparation of propionic acid were as follows: catalyst amount of 3 mol%, n(H_2O_2):n(1-propanol) ratio of 3:1, reaction temperature of 60 °C, and reaction time of 8 h. Under the selected optimised conditions, the conversion of 1-propanol was 88%, and the selectivity of propionic acid reached 75%.

Proposed catalytic mechanism

According to the reaction results obtained herein and those reported previously [34], the proposed catalytic mechanism for the oxidation of 1-propanol catalysed by



Scheme 1 Proposed mechanism of the catalytic oxidation of 1-propanol

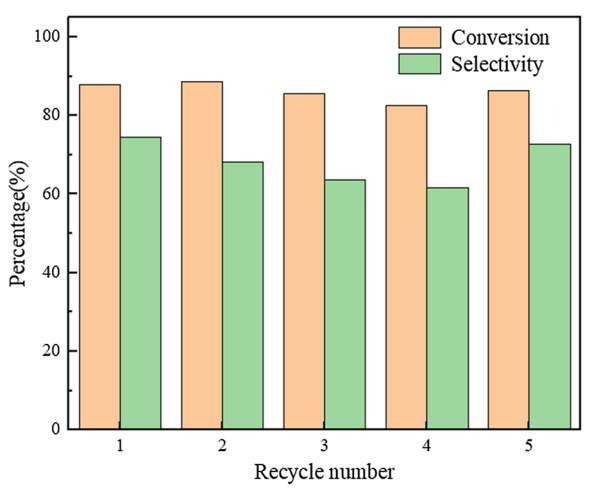


Fig. 10 Reuse performance of the catalyst

$(ProH)_3[PW_{12}O_{40}]$ is shown in Scheme 1. In the oxidation process, the catalyst $(ProH)_3[PW_{12}O_{40}]$ first reacts with H_2O_2, and the heteropoly anion of the catalyst is depolymerized to a smaller active peroxygen intermediate. This intermediate (the active centre) subsequently oxidises the substrate 1-propanol to propionaldehyde, which is further oxidised to propionic acid. The kinetic curves of the reaction at different reaction times (Fig. 8) revealed that with increasing reaction time, the selectivity of propionaldehyde decreased and the selectivity of propionic acid gradually increased, indicating that 1-propanol was first oxidised to propionaldehyde and then to propionic acid. Nonetheless, the formation of propionaldehyde and its oxidation can simultaneously proceed. After the oxidation reaction, the active intermediate loses active oxygen and re-polymerises into the original Keggin structure.

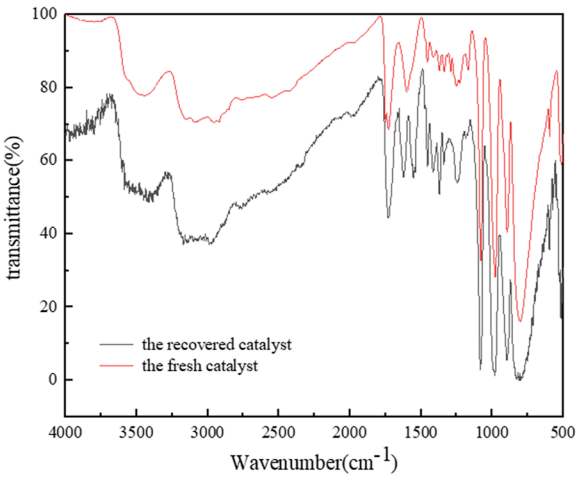


Fig. 11 FT-IR spectra of the fresh and recovered catalysts

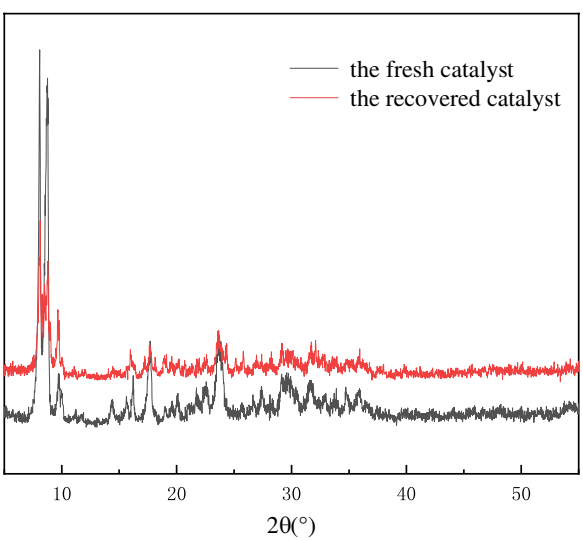


Fig. 12 XRD patterns of the fresh and recovered catalysts

Reuse of the catalyst

After the reaction, the catalyst was recovered by centrifugation. Figure 10 shows the cycling performance of $(ProH)_3[PW_{12}O_{40}]$ for catalysing the oxidation of 1-propanol under the optimised conditions. Over the first four cycles, the conversion of 1-propanol and the selectivity of propionic acid gradually declined. However, the conversion remained at >80%, and the selectivity was >60%. After four cycles, the recovered catalyst was characterised by FT-IR (Fig. 11) and XRD (Fig. 12). Compared with the fresh catalyst, the structure of the recovered catalyst was not destroyed in the first four cycles, indicating good stability. The decrease in catalytic activity may be due to a slight loss of the catalyst during

Table 2 The oxidation of different primary alcohols catalysed by $(ProH)_3[PW_{12}O_{40}]$

Entry	Substrate	Product	Conversion /%	Yield /%	Selectivity /%
1	1-propanol	Propionic acid	87.96	65.62	74.61
2	1-butanol	Butyric acid	85.56	61.38	71.74
3	1-pentanol	Pentanoic acid	82.61	54.03	65.76
4	1-hexanol	Hexanoic acid	80.23	50.87	63.41
5	Benzyl alcohol	Benzyl acid	81.02	63.09	77.87

Reaction conditions: n(substrate) = 10 mmol, n(catalyst) = 0.3 mmol, $n(30\%H_2O_2)$ = 30 mmol, 60 °C, 8 h

separation. For the fifth cycle, an equivalent amount of the lost catalyst was added, and catalytic activity was restored (Fig. 10).

Substrate expansion

The catalytic performance of the $(ProH)_3[PW_{12}O_{40}]$ catalyst in the oxidation of other primary alcohols was also investigated; the results are shown in Table 2. The $(ProH)_3[PW_{12}O_{40}]$ catalyst exhibits good catalytic activity for various aliphatic primary alcohols and aromatic benzyl alcohol. All the reactions have high conversions, with the corresponding acids being the primary oxidation product. The selectivity of acids can be further improved by optimising the catalytic conditions. Therefore, $(ProH)_3[PW_{12}O_{40}]$ as a catalyst for the selective oxidation of primary alcohols to the corresponding acids by H_2O_2 has good substrate adaptability.

Conclusions

Proline-based heteropolyoxometalate $(ProH)_3[PW_{12}O_{40}]$ has been successfully used to catalyse the selective oxidation of 1-propanol toward propionic acid with H_2O_2 as the oxidant. The conversion of 1-propanol and the selectivity of propionic acid reached 88% and 75%, respectively. The excellent catalytic activity of $(ProH)_3[PW_{12}O_{40}]$ is attributed to its high capacity as an oxygen transfer agent with a suitable acidity. $(ProH)_3[PW_{12}O_{40}]$ also exhibited good recycling efficiency. This study provides a new preparation method for propionic acid via a green route, and the developed catalyst shows immense potential for the selective oxidation of other primary alcohols to the corresponding carboxylic acids with H_2O_2 as an oxidant.

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Not applicable.

Authors' contributions

FY and SY conceived the study and were in charge of overall direction and planning. ML performed the whole chemical experiments. BY and CX directed the analysis of the data. FY and SY were major contributors in writing the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analysed during this study are included in this published article.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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References

1. Stowers CC, Cox BM, Rodriguez BA (2014) Development of an industrializable fermentation process for propionic acid production. J Ind Microbiol Biot 41(5):837–852
2. Liu L, Zhuge X, Shin HD, Chen RR, Li J, Du G, Chen J (2015) Improved production of propionic acid in propionibacterium jensenii via combinational overexpression of glycerol dehydrogenase and malate dehydrogenase from Klebsiella pneumoniae. Appl Environ Microbiol 81(7):2256–2264
3. Reichardt N, Duncan SH, Young P, Belenguer A, McWilliam Leitch C, Scott KP, Flint HJ, Louis P (2014) Phylogenetic distribution of three pathways for propionate production within the human gut microbiota. ISME J 8(6):1323–1335
4. Louis P, Hold GL, Flint HJ (2014) The gut microbiota, bacterial metabolites and colorectal cancer. Nat Rev Microbiol 12(10):661–672
5. Gong J, Flaherty DW, Yan T, Mullins CB (2008) Selective oxidation of propanol on Au(III): mechanistic insights into aerobic oxidation of alcohols. ChemPhysChem 9(17):2461–2466
6. Enache DI, Knight DW, Hutchings GJ (2005) Solvent-free oxidation of primary alcohols to aldehydes using supported gold catalysts. Catal Lett 103(12):43–52
7. Wang SS, Yang GY (2015) Recent advances in polyoxometalate-catalyzed reactions. Chem Rev 115(11):4893–4962
8. Zhao M, Zhang XW, Wu CD (2017) Structural transformation of porous polyoxometalate frameworks and highly efficient biomimetic aerobic oxidation of aliphatic alcohols. ACS Catal 7(10):6573–6580
9. Wang Y, Wu ZK, Yu H, Han S, Wei YG (2020) Highly efficient oxidation of alcohols to carboxylic acids using a polyoxometalate-supported chromium(III) catalyst and CO_2. Green Chem 22(10):3150–3154

10. Guo Z, Liu B, Zhang Q, Deng W, Wang Y, Yang Y (2014) Recent advances in heterogeneous selective oxidation catalysis for sustainable chemistry. Chem Soc Rev 43(10):3480–3524
11. Ribeiro SO, Juliao D, Cunha-Silva L, Domingues VF, Valença R, Ribeiro JC, de Castro B, Balula SS (2016) Catalytic oxidative/extractive desulfurization of model and untreated diesel using hybrid based zinc-substituted polyoxometalates. RSC Adv 166(15):268–275
12. Yu FL, Wang YY, Liu CY, Xie CX, Yu ST (2014) Oxidative desulfurization of fuels catalyzed by ammonium oxidative-thermoregulated bifunctional ionic liquids. Chem Eng J 255:372–376
13. Talsi EP, Ottenbacher RV, Bryliakov KP (2015) Bioinspired oxidations of aliphatic C-H groups with H_2O_2 in the presence of manganese complexes. J Organomet Chem 793:102–107
14. Omwoma S, Gore CT, Ji YC, Hu CW, Song YF (2015) Environmentally benign polyoxometalate materials. Coord Chem Rev 286:17–29
15. Zhou Y, Guo ZJ, Hou W, Wang Q, Wang J (2015) Polyoxometalate-based phase transfer catalysis for liquid-solid organic reactions: a review. Catal Sci Technol 5:4324–4335
16. Vilanculo CB, da Silva MJ, Teixeira MG, Villarreal JA (2020) One-pot synthesis at room temperature of epoxides and linalool derivative pyrans in monolacunary $Na_7PW_{11}O_{39}$-catalyzed oxidation reactions by hydrogen peroxide. RSC Adv 10(13):7691–7697
17. Lü H, Li P, Liu Y, Hao L, Ren W, Zhu W, Deng C, Yang F (2017) Synthesis of a hybrid Anderson-type polyoxometalate in deep eutectic solvents (DESs) for deep desulphurization of model diesel in ionic liquids (ILs). Chem Eng J 3(13):1004–1009
18. Liu R, Chen J, Chen L, Guo Y, Zhong J (2014) One-step approach to 2,5-diformylfuran from fructose by using a bifunctional and recyclable acidic polyoxometalate catalyst. ChemPlusChem 79(10):1448–1454
19. da Silva MJ, da Silva Andrade PH, Ferreira SO, Vilanculo CB, Oliveira CM (2018) Monolacunary $K_8SiW_{11}O_{39}$-catalyzed terpenic alcohols oxidation with hydrogen peroxide. Catal Lett 148(8):2516–2527
20. Lan J, Lin J, Chen Z, Yin G (2015) Transformation of 5-hydroxymethylfurfural (HMF) to maleic anhydride by aerobic oxidation with heteropolyacid catalysts. ACS Catal 5(4):2035–2041
21. Lachkar D, Vilona D, Dumont E, Lelli M, Lacote E (2016) Grafting of secondary diolamides onto $[P_2W_{15}V_3O_{62}]^{9-}$ generates hybrid heteropoly acids. Angew Chem Int Ed Engl 55(20):5961–5965
22. Coronel NC, da Silva MJ, Ferreira SO, da Silva RC, Natalino R (2019) $K_5PW_{11}NiO_{39}$-catalyzed oxidation of benzyl alcohol with hydrogen peroxide. ChemistrySelect 4(1):302–310
23. Ding Y, Zhao W (2011) The oxidation of pyridine and alcohol using the Keggin-type lacunary polytungstophosphate as a temperature-controlled phase transfer catalyst. J Mol Catal A: Chem 337(12):45–51
24. Tundo P, Romanelli GP, Vázquez PG, Aricò F (2010) Multiphase oxidation of alcohols and sulfides with hydrogen peroxide catalyzed by heteropolyacids. Catal Commun 11(15):1181–1184
25. Jing L, Shi J, Zhang F, Zhong Y, Zhu W (2013) Polyoxometalate-based amphiphilic catalysts for selective oxidation of benzyl alcohol with hydrogen peroxide under organic solvent-free conditions. Ind Eng Chem Res 52(30):10095–10104
26. Bhattacharjee D, Sutradhar D, Chandra AK, Myrboh B (2017) L-proline as an efficient asymmetric induction catalyst in the synthesis of chromeno[2,3-d]pyrimidine-triones, xanthenes in water. Tetrahedron 73(25):3497–3504
27. Karthikeyan P, Aswar SA, Muskawar PN, Sythana SK, Bhagat PR, Kumar SS, Satvat PS (2016) A novel *L*-amino acid ionic liquid for quick and highly efficient synthesis of oxime derivatives-An environmental benign approach. Arab J Chem 9(2):1036–1039
28. Tang F, Zhang Q, Ren D, Nie Z, Liu Q, Yao S (2010) Functional amino acid ionic liquids as solvent and selector in chiral extraction. J Chromatogr A 1217(28):4669–4674
29. Pizzio LR, Vázquez PG, Cáceres CV, Blanco MN (2003) Supported Keggin type heteropolycompounds for ecofriendly reactions. Appl Catal A 256(1–2):125–139
30. Yu FL, Chi YJ, Gao C, Chen RR, Xie CX, Yu ST (2020) Baeyer-Villiger oxidation of cyclic ketones catalyzed by amino acid ionic liquids. Chem Res Chinese Universities 36(5):865–869
31. Tan R, Li CY, Luo JQ, Kong Y, Zheng WG, Yin DH (2013) An effective heterogeneous l-proline catalyst for the direct asymmetric aldol reaction using graphene oxide as support. J Catal 298:138–147
32. Pizzio L, Vazquez P, Caceres C, Blanco M, Thomas H, Alesso E, Lantano B, Finkielsztein L, Moltrasio G (2000) Silica-supported heteropolyacids as catalysts in alcohol dehydration reactions. J Mol Cata A: Chem 161(1–2):223–232
33. Zhou YS, Mei XY, Cai Z, Wang Q, Duanmu JH, Kai OY, Zhang HJ, Tang XJ, Han XX (2021) An efficient and recyclable Sn-based phosphotungstic acid with tunable Bronsted/Lewis acidity for selective oxidation of benzyl alcohol. J Brazil Chem Soc 32(1):158–169
34. Pope MT, Dickman MH (1994) Peroxo and superoxo complexes of chromium, molybdenum, and tungsten. Chem Rev 94(3):569–584

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