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Article

Selective oxidation of alcohols over copper zirconium phosphate

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ABSTRACT

The catalytic activity of copper zirconium phosphate (ZPCu) in the selective oxidation of alcohols to their corresponding ketones or aldehydes, using H_2O_2 as an oxidizing agent, was studied. The oxidation reaction was performed without any organic solvent, phase-transfer catalyst, or additive. Steric factors associated with the substrates influenced the reaction. The catalyst was characterized using X-ray diffraction, inductively coupled plasma atomic emission spectroscopy, energy-dispersive X-ray spectroscopy, and scanning electron microscopy. It was shown that the interlayer distance increased from 0.74 to 0.80 nm and the crystallinity was reduced after Cu^{2+} intercalation into the layers. This catalyst can be recovered and reused three times without significant loss of activity and selectivity.

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1. Introduction

α -Zirconium phosphate (ZP) is one of the most important inorganic compounds with a layered structure, and it has been used in many fields [1,2]. ZP is a useful ion-exchanger because of its extreme insolubility in water, high thermal stability, and resistance to radiation and abrasion [3,4]. The H^+ of the P–OH is the exchangeable site and can be exchanged for divalent or trivalent cations, with appropriate enlargement of the interlayer distance [5–9]. There have been some reports on the catalytic activities of these ion-exchanged materials [9–14].

The selective oxidation of alcohols to the corresponding carbonyl compounds is one of the most important and widely used functional group transformations in fundamental synthetic research and industrial manufacturing. This is because of the extensive use of aldehydes and ketones in the synthesis of various chemicals, vitamins, drugs, and fragrances [15–19]. Benzaldehyde (BzH), which is a typical product of alcohol oxidation, is an important starting material for the preparation of

intermediates in the dyestuff, agrochemicals, perfumery, and pharmaceutical industries [18–20]. Various catalysts have been developed for the oxidation of alcohols, using molecular O_2 or aqueous H_2O_2 as the oxidant, in the presence and/or absence of solvents [15–26]. In the present work, we report an efficient, convenient, and mild procedure for the selective oxidation of alcohols by copper zirconium phosphate (ZPCu); the catalyst was characterized using inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD), and scanning electron microscopy (SEM).

2. Experimental

2.1. Catalyst synthesis

All chemicals and solvents were purchased from the Merck Chemical Company and used without further purification. The detailed procedure for the preparation of the catalyst can be found in the literature [2,7–9]; some modifications were made

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to the procedure. ZP was prepared as follows. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (5 g) was refluxed in 12 mol/L H_3PO_4 (50 mL) at 100 °C for 24 h. The obtained precipitate was filtered off and washed with 0.1 mol/L H_3PO_4 until free of Cl^- . Finally, the solid was washed several times with distilled water until the pH was neutral, and dried in an oven at 110 °C for 24 h [2]. The final product was ground into a fine powder and its structure was determined using XRD. ZPCu was prepared using an ion-exchange reaction [7–9]. ZP (3 g) was dispersed in deionized water (50 mL) at 50 °C. $\text{Cu}(\text{OAc})_2$ solution (0.1 mol/L, 100 mL, excess of Cu^{2+}) was added to the dispersion and it was refluxed for 4 d. The acetate ion effectively acts as a base to keep the hydrogen ion concentration in the solution low enough to achieve high loadings [6]. Complete exchange between the cations and the hydrogens of the P–OH groups cannot be achieved in less than 3 d or below 80 °C [27]. The slurry was hot filtered, and the obtained light-blue solid was washed with distilled water until no Cu^{2+} was detected in the washing solution (the filtrate was colorless). Finally, the product was dried at 100 °C for 24 h and calcined at 600 °C for 5 h. The final pale-blue product, copper zirconium phosphate $\text{CuZr}(\text{PO}_4)_2$, was denoted by ZPCu (Scheme 1).

2.2. General experimental procedure for oxidation reaction

A substrate (5 mmol) and ZPCu (5 mol%) were added to a 25 mL two-necked flask. The flask was heated in an oil bath to 60 °C and then 30% H_2O_2 (0.015 mol) was added slowly, with continuous stirring, over a specified time. The reaction progress was monitored using gas chromatography (GC). When the reaction was complete, the reaction mixture was cooled to room temperature and the catalyst was removed by centrifugation. The organic layer was then separated from the aqueous phase by extraction with *n*-hexane and dried over anhydrous CaCl_2 . The reaction products were identified GC-mass spectrometry (MS) and ^1H nuclear magnetic resonance (NMR) spectroscopy.

3. Results and discussion

3.1. Catalyst characterization

The chemical compositions of ZPCu samples obtained at different stages of the catalyst synthesis (before and after the catalytic reaction) were determined using ICP-AES (PerkinElmer ICP-AES 7300 dv spectrometer). The results are shown in Table 1. Energy-dispersive X-ray spectroscopy (EDS; Zeiss EVO, operated at 20 kV) was also used to determine the chem-

Scheme 1. Summary of ZPCu preparation.

Table 1

Elemental contents of copper zirconium phosphates.

Entry	Sample	Elemental content (atm%)			
		Cu	O	Zr	P
1	ZP	—	63.1	13.6	23.3
2	ZPCu	11.7	58.7	10.9	18.8
3	ZPCu ^a	11.1	57.6	11.6	19.7
4	ZPCu ^b	11.5	59.3	10.5	18.7
5	ZPCu ^c	8.6	62.1	11.7	17.6

^a From EDS analysis. ^b After run 1. ^c After run 4.

ical composition of ZPCu. The results are shown in Fig. 1 and Table 1 (entry 3).

The results were comparable with earlier one [4,8,9]. There was negligible leaching of copper ions into the reaction medium (after first use).

Figure 2 shows the powder XRD (Philips X'pert) patterns of the prepared ZP and ZPCu. They show characteristic reflections in the 2θ range 0°–40°. The diffraction peak of ZP at $\sim 12^\circ$ was assigned to a d_{002} planar basal spacing of 0.75 nm, which was consistent with the previously reported patterns of ZP and derivatives, with a hexagonal crystal system [2]. Figure 2 shows that the d -spacing of the (002) plane of ZPCu was larger, which implies that Cu^{2+} intercalated into the ZP interlayers and increased the d_{002} basal interlamellar spacing of ZP from 0.75 to 0.80 nm.

It is well known that the radii of Cu^{2+} (0.072 nm) [28,29] and hydrated Cu^{2+} (0.419 nm) [30] are smaller than the basal spacing of ZrP (0.75 nm). Cu^{2+} was therefore inserted into the ZP interlayers, increasing the basal spacing of the modified ZP

Fig. 1. EDS spectrum of ZPCu sample.

Fig. 2. XRD patterns of powder ZP and ZPCu.

Fig. 3. SEM images of prepared ZP (a) and ZPCu (b, c) samples.

after ion exchange [7–9]. We concluded from the above data that ZPCu was formed. The surface morphologies of ZP and ZPCu were studied using SEM (Philips XL). As shown in Fig. 3, ZP shows hexagonal plates and disks with well-defined shapes and very smooth surfaces. For ZPCu catalyst, it is much less ordered than ZP and found some aggregation of ZPCu particles in sheets and spheres, and conglomerates with uneven shapes and sizes.

3.2. Oxidation reaction and expected mechanism

Benzyl alcohol (BzOH) was selected as the model substrate for determining the optimum conditions; the results are summarized in Table 2. Although the major product was BzH, benzoic acid was also formed as a side product (Table 2, entries 3, 6, 9, 11, 12). It was found that the selectivity and/or yield were changed by the reaction parameters, i.e., time (Table 2, entries 1–3), molar ratio (Table 2, entries 4–6), temperature (Table 2, entries 7–9), or molar percentage of catalyst (Table 2, entries 10–12). It shows that increasing the temperature initially accelerated the reaction (up to 60 °C), but further increases resulted in a decrease in the yield, possibly because of self-de-

composition of H₂O₂ at high temperatures, leading to insufficient oxidation of BzOH (Table 2, entries 2 and 7–9). When the molar ratio of BzOH:H₂O₂ reached 1:3, the highest yield was obtained, but on further increasing the ratio, the yield increased slightly, but the selectivity for BzH decreased sharply (Table 2, entries 2 and 4–6). The optimum reaction conditions were 60 °C, 1:3 of BzOH:H₂O₂ molar ratio, 90 min (Table 2, entry 2). The oxidation reaction was also performed using ZP as the catalyst (Table 2, entry 13) and without a catalyst (Table 2, entry 14) to investigate the role of our catalyst. In both cases, no significant amount of BzH was detected.

As shown in Table 3, a wide range of alcohols bearing either electron-donating or electron-withdrawing groups were successfully oxidized to their corresponding carbonyl compounds, in short reaction times, using ZPCu. Efficient transformations of

Table 2
Optimization of reaction conditions for BzOH oxidation.

Entry	Time (min)	Molar ratio ^a	Temperature (°C)	Catalyst (mol%)	Yield ^b (%)	Selectivity ^c (%)
1	60	1:3	60	5	73	>99
2	90	1:3	60	5	90	>99
3	120	1:3	60	5	93(84)	75(25)
4	90	1:1	60	5	45	>99
5	90	1:2	60	5	62	>99
6	90	1:4	60	5	96(92)	67(37)
7	120	1:3	r.t.	5	13	>99
8	120	1:3	40	5	48	>99
9	90	1:3	80	5	79(86)	71(29)
10	90	1:3	60	1	54	>99
11	90	1:3	60	10	92(84)	78(22)
12	90	1:3	60	15	82(90)	65(35)
13 ^d	120	1:2	60	5	2	>99
14	90	1:3	60	—	—	—

^a BzOH:H₂O₂ molar ratio.

^b Isolated yield for BzH (benzoic acid as the main by-product).

^c Selectivity for BzH (benzoic acid as the main by-product).

^d ZP was used as the catalyst (blank).

Table 3
Oxidation reaction in presence of ZPCu.

Entry	R ₁	R ₂	Time (min)	Molar ratio ^a	Yield ^b (%)	Selectivity (%)
1	Ph	H	90	1:3	90	>99
2	2-MeO-C ₆ H ₄	H	60	1:3	79	>99
3	4-MeO-C ₆ H ₄	H	60	1:3	96	>99
4	4-Me-C ₆ H ₄	H	60	1:3	91	>99
5	2-Cl-C ₆ H ₄	H	60	1:3	81	>99
6	4-Cl-C ₆ H ₄	H	60	1:3	93	>99
7	2-Br-C ₆ H ₄	H	60	1:3	78	>99
8	4-Br-C ₆ H ₄	H	60	1:3	95	>99
9	2-NO ₂ -C ₆ H ₄	H	60	1:3	79	>99
10	4-NO ₂ -C ₆ H ₄	H	60	1:3	97	>99
11	4-NC-C ₆ H ₄	H	60	1:3	95	>99
12	1-Naphthyl	H	60	1:3	93	>99
13	2-Naphthyl	H	60	1:3	94	>99
14	PhCH=CH	H	60	1:3	92	>99
15	Ph	Ph	150	1:3	75	>99
16	Ph	CH ₃	150	1:3	79	>99
17	4-MeO-C ₆ H ₄	CH ₃	120	1:3	84	>99
18	4-Me-C ₆ H ₄	CH ₃	120	1:3	85	>99
19	4-Cl-C ₆ H ₄	CH ₃	120	1:3	84	>99
20	4-Br-C ₆ H ₄	CH ₃	120	1:3	86	>99
21	4-NO ₂ -C ₆ H ₄	CH ₃	120	1:3	89	>99
22	CH ₃ CH ₂ CH ₂	H	180	1:4	76	>99
23	CH ₃ CH ₂	CH ₃	180	1:4	72	>99
24	CH ₃ (CH ₂) ₄	H	180	1:4	78	>99
25	Cyclohexanol	Cyclohexanone	180	1:4	73	>99

^a Substrate:H₂O₂ molar ratio.

^b Isolated yield. All products were identified by their GC-MS and ¹H NMR spectra with authentic samples [13–16].

Scheme 2. Proposed mechanism for ZPCu/H₂O₂ catalytic system.

primary alcohols to the desired aldehydes were achieved without any over-oxidation to the corresponding carboxylic acids (Table 3, entries 1–14).

Electron-donating and electron-withdrawing groups accelerated the oxidation reaction, but the yields obtained using *ortho*-substituted substrates (Table 3, entries 2, 5, 7, and 9) were lower than those obtained with the corresponding *para* isomer, because of steric hindrance [19,31,32]. Based on these observations, a proposed mechanism for the ZPCu-catalyzed oxidation of alcohols with H₂O₂ is shown in Scheme 2. First, the Cu Lewis acid site (on the ZPCu surface) interacts with H₂O₂ to form I, which reacts with the alcohol to give intermediate II. Two hydration steps convert II to the corresponding carbonyl compound, with regeneration of the active sites. Steric hindrance around the hydroxyl group of the alcohol, caused by the presence of substituents at the *ortho* position (Table 3, entries 2, 5, 7, and 9) or the use of more hindered secondary alcohols (Table 3, entries 15–21), results in longer reaction times and lower yields. Similar behavior has been previously reported [19,31,32].

Spent ZPCu was recovered from the reaction medium and reused, to examine the catalyst recyclability. For recycling, the catalyst was separated from the reaction mixture by centrifugation after first use, washed successively with ethanol and water, dried at 110 °C for 2 h, and activated at 500 °C for 2 h. The product yields obtained with spent ZPCu were similar to those obtained with the fresh catalyst up to the fourth cycle (Table 4). The chemical composition of the regenerated catalyst was determined by elemental analysis after each reaction (Table 1, entries 4 and 5). No significant changes in the composition or the environment were observed after regeneration until the fourth cycle.

All products were identified by comparison of their GC-MS (Agilent 5975C) and ¹H NMR spectra (Bruker-Avance AQS 400 MHz spectrometer; in CDCl₃) with those of authentic samples

[13–16]. ¹H NMR spectroscopic data of compounds from Table 3 are as follows.

PhCHO (Table 3, entry 1): δ = 10.01 (s, 1H), 7.85–7.45 (m, 5H).

2-MeOC₆H₄CHO (Table 3, entry 2): δ = 10.41 (s, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.6–7.54 (m, 1H), 7.07–7.0 (m, 2H), 3.96 (s, 3H).

4-MeOC₆H₄CHO (Table 3, entry 3): δ = 9.90 (1H, s), 7.85 (2H, d, *J* = 8.7 Hz), 7.0 (2H, d, *J* = 8.4 Hz), 3.93 (3H, s).

4-MeC₆H₄CHO (Table 3, entry 4): δ = 9.92 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 2.43 (s, 3H).

2-ClC₆H₄CHO (Table 3, entry 5): δ = 10.40 (s, 1H), 7.88–7.86 (q, 1H), 7.54–7.31 (m, 3H).

4-ClC₆H₄CHO (Table 3, entry 6): δ = 9.98 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H).

2-BrC₆H₄CHO (Table 3, entry 7): δ = 10.38 (s, 1H), 7.91–7.88 (m, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.47–7.42 (m, 2H).

4-BrC₆H₄CHO (Table 3, entry 8): δ = 10.0 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H).

2-NO₂C₆H₄CHO (Table 3, entry 9): δ = 10.44 (s, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 7.98–7.96 (m, 1H), 7.84–7.76 (m, 2H).

4-NO₂C₆H₄CHO (Table 3, entry 10): δ = 10.18 (s, 1H), 8.39 (d, *J* = 8.7 Hz, 2H), 8.08 (d, *J* = 8.2 Hz, 2H).

4-NCC₆H₄CHO (Table 3, entry 11): δ = 10.13 (s, 1H), 8.11 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H).

1-Naphthaldehyde (Table 3, entry 12): δ = 10.39 (s, 1H), 9.24 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 7.3 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.65–7.56 (m, 2H).

2-Naphthaldehyde (Table 3, entry 13): δ = 10.17 (1H, s), 8.35 (s, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.98 (dd, *J* = 1.3 Hz, 10.0 Hz, 2H), 7.94 (dd, *J* = 8.7 Hz, 14.2 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.61 (dd, *J* = 7.6 Hz, 1H).

PhCH=CHCHO (Table 3, entry 14): δ = 9.67 (d, *J* = 7.6 Hz, 1H), 7.56–7.52 (m, 2H), 7.46–7.41 (m, 4H), 6.72–6.66 (m, 1H).

Ph₂CO (Table 3, entry 15): δ = 7.81 (d, *J* = 7.5 Hz, 4H), 7.59 (t, *J* = 7.3 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 4H).

C₆H₅COCH₃ (Table 3, entry 16): δ = 7.97 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 2.62 (s, 3H).

4-MeOC₆H₄COCH₃ (Table 3, entry 17): δ = 7.90 (d, *J* = 9.0 Hz, 2H), 6.9 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H), 2.58 (s, 3H).

4-MeC₆H₄COCH₃ (Table 3, entry 18): δ = 7.84 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.57 (s, 3H), 2.38 (s, 3H).

4-ClC₆H₄COCH₃ (Table 3, entry 19): δ = 7.92–7.88 (d, *J* = 8.4 Hz, 2H), 7.45–7.42 (d, *J* = 8.4 Hz, 2H), 2.58 (s, 3H).

4-BrC₆H₄COCH₃ (Table 3, entry 20): δ = 7.84–7.81 (d, *J* = 8.5 Hz, 2H), 7.63–7.6 (d, *J* = 8.5 Hz, 2H), 2.57 (s, 3H).

4-NO₂C₆H₄COCH₃ (Table 3, entry 21): δ = 8.35–8.33 (d, *J* = 8.4 Hz, 2H), 8.15–8.12 (d, *J* = 8.4 Hz, 2H), 2.7 (s, 3H).

CH₃CH₂CH₂CHO (Table 3, entry 22): δ = 9.76 (s, 1H), 2.39 (m, 2H), 1.65 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

CH₃CH₂CHOCH₃ (Table 3, entry 23): δ = 2.47 (q, *J* = 7.6 Hz, 2H), 2.14 (s, 3H), 1.14 (t, *J* = 7.6 Hz, 3H).

CH₃(CH₂)₄CHO (Table 3, entry 24): δ = 9.81 (s, 1H), 2.38 (m, 2H), 1.65 (m, 2H), 1.34 (m, 2H), 1.29 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H).

Cyclohexanone (Table 3, entry 25): δ = 2.52–2.38 (m, 4H), 2.2–1.64 (m, 6H).

Table 4

Catalyst reuse under optimum reaction conditions for oxidation of BzOH.

Fresh	run 1	run 2	run 3	run 4
90	90	87	84	70

Reaction conditions: BzOH 5 mmol, H₂O₂ 0.015 mol, catalyst 5 mol%, 60 °C, 90 min.

Graphical Abstract

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Selective oxidation of alcohols over copper zirconium phosphate

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Copper zirconium phosphate was prepared and used as an efficient catalyst for the selective oxidation of various alcohols to the corresponding aldehydes and ketones, in good yields and with excellent selectivities.

4. Conclusions

In summary, we have reported the catalytic performance of water-insoluble ZPCu in the oxidation of alcohols using H₂O₂. The catalyst was characterized using various methods and the results showed good agreement with those in the literature. ZPCu showed outstanding catalytic performance with excellent conversion of BzOH and selectivity for BzH at 60 °C for 90 min. The selectivity remained unchanged in all the reactions, although the conversions were affected by steric hindrance; alcohols with bulky groups required longer reaction times. This procedure is environmentally benign, general, efficient, high yielding, safe, and operationally simple.

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