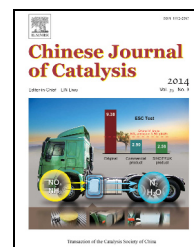


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Article

Selective oxidation of alcohols over copper zirconium phosphate

Abdol R. Hajipour^{a,b,*}, Hirbod Karimi^a^a *Pharmaceutical Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156, Iran*^b *Department of Neuroscience, University of Wisconsin, Medical School, Madison, WI 53706-1532, USA*

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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 H₂O₂ 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 Cu²⁺ 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 O₂ or aqueous H₂O₂ 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

* Corresponding author. Tel: +98-311-3913262; Fax: +98-311-3913252; E-mail: haji@cc.iut.ac.ir

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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-

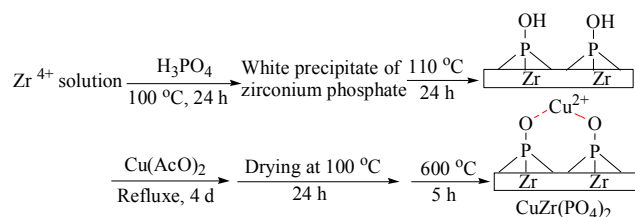


Table 1
Elemental contents of copper zirconium phosphates.

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 ~12° 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

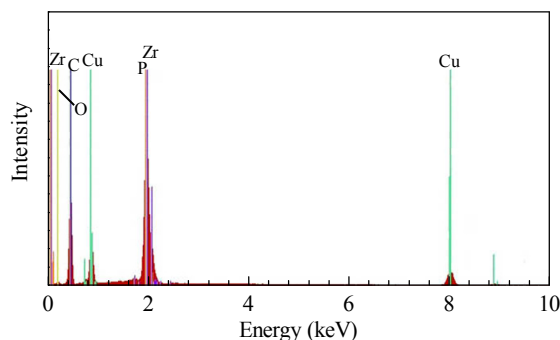


Fig. 1. EDS spectrum of ZPCu sample.

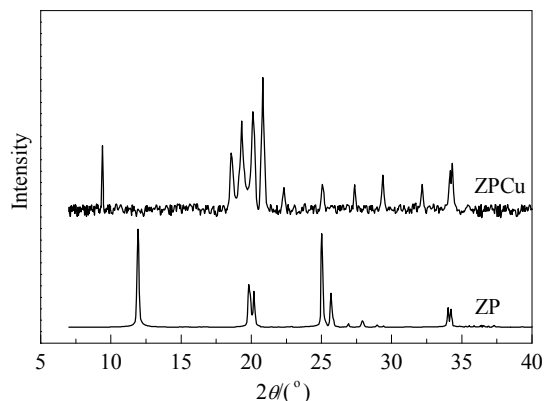


Fig. 2. XRD patterns of powder ZP and ZPCu.

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