



# Characterization and catalytic performances of copper and cobalt-exchanged hydroxyapatite in glycerol conversion for 1-hydroxyacetone production

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## ABSTRACT

Calcium hydroxyapatites (HAP) containing cobalt or copper were synthesized and catalytically evaluated in the dehydration of glycerol for valuable chemical intermediates production. The solids were characterized by chemical analysis, X-ray diffraction (XRD), Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS), acid-base measurements, Raman spectroscopy and nitrogen adsorption–desorption isotherms. Cobalt-containing HAPs had the characteristic hydroxyapatite ( $\text{Ca}_{10-x}(\text{HPO}_4)(\text{PO}_4)_{6-x}(\text{OH})_{2-x}(\text{H}_2\text{O})_x$ ) and monetite  $\text{Ca}(\text{HPO}_4)$  phases, independently of the cobalt contents, being mesoporous materials. This was proven to be due to  $\text{Ca}^{2+}$  ions replaced by  $\text{Co}^{2+}$  ones in HAP structure; since the cobalt amount increased, a dispersion of nanosized cobalt species was suggested. Copper-containing hydroxyapatites showed the HAP and monetite phases. Increased copper contents provided the ionic exchange of  $\text{Ca}^{2+}$  by  $\text{Cu}^{2+}$  and resulted in the libethenite ( $\text{Cu}_2(\text{OH})(\text{PO}_4)$ ) phase formation as well as the deposition of  $\text{CuO}$  on solid surface. These solids possessing distinct morphologies had micro and mesopores and preserved the HAP and monetite phases, even increasing the copper content. The catalytic evaluation in the dehydration of glycerol was dependent on the content of the metals as well as the nature of the active phase. Generally, copper-containing samples were more active than those possessing cobalt, probably due to the either stable libethenite phase presence or great acidity of the formers. The catalytic performance of the solids with low copper contents showed the elevated selectivity to 1-hydroxyacetone and products from its dimerization–cyclisation reactions whereas samples possessing cobalt were selective to 1-hydroxyacetone and light products.

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## 1. Introduction

Selective conversion of alcohols to value-added chemicals is an important transformation in synthetic chemistry. The conversion of biomass-derived glycerol tri-alcohol is highly desirable from environmental and technical points of view, due to potentially environmental impact and the relatively low cost of raw glycerol [1–6]. Dehydration of glycerol reaction fulfils these requirements of green chemistry, being an attractive route to produce 1-hydroxyacetone (acetol) and 2-propenal (acrolein) [3,5]. These chemicals are

important intermediates in a large number of industrial processes such as acrylic acid esters, agrochemicals and superabsorbent production as well as polymers and detergents, among others [6,7].

The use of harsh conditions to the reaction allows for elevated yields of acetol and acrolein and over appropriate catalysts can generate 1,2-propanediols, allyl alcohols and heavy compounds [4–7]. In addition, various heterogeneous catalysts have been studied in the dehydration of glycerol including sulfates and phosphates impregnated on oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{--Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ), molecular sieves, other types of mixed oxides ( $\text{CeO}_2$ ,  $\text{CuO}$ ,  $\text{SnO}_2$ ,  $\text{WO}_3$ ,  $\text{Mo}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CrO}_3$ ) and heteropolyacids or metals supported on oxides and zeolites as well [1–10]. It has been suggested that the acid sites participate in the activation of glycerol with respect to acrolein selectivity, especially for Brønsted sites. Whereas the selectivity to acetol is associated to the presence of

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either Lewis acid sites or base sites on solid surface [1,6–9]. However, there is no direct correlation between the selectivity of acetol and basicity of the solids or yet the role played by the acidity of Lewis sites is not a consensus in the open literature. In addition, the structural properties of the support action and nature of its interactions with the active phase have not been established in glycerol conversion.

Currently, dehydration of alcohols over acid phosphate catalysts has been studied and the action of the Lewis sites for acetol production is well described [1,6,8]. Thus, the efficiency of divalent (Cu, Ca, Co) and trivalent cations (Ce, Fe, La) as Lewis sites dispersed on phosphated alumina or silica has been shown to decrease the acidity of the solids during the reaction [9,11]. Indeed, the aforesaid cations promoted the creation of new types of acid sites due to the carboxylic species formation from glycerol and allowing high yields for acetol. Another factor to be pointed out is the structural properties of the phosphates governing the reducibility of the oxides and phase transformations, which in turn, influences on the distribution of the products formed, as the reaction proceeds [1,8,11, (and references herewith)]. These results indicate that the combination of Brønsted sites and Lewis centers, both of which are active catalytic sites in hydroxyapatites and oxides, respectively, would enhance the activity of the catalysts for the dehydration of glycerol. Moreover, little attention has been paid to the durability and the structural changes of the modified hydroxyapatites under the mild reaction conditions.

The present work is devoted to investigate the effect of different hydroxyapatites on the dehydration of glycerol with varying the copper and cobalt amounts. Calcium hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) is one of the most important constituent of bones and teeth enamel and is widely used in biomedical engineering, adsorbents, ion exchangers and catalysts [12–16]. The unique structural features and compositions of these phosphates e.g., the Ca/P ratio, porosity and crystallinity hold interesting possibility in transformation of alcohols reactions due to the acid-base and redox properties of the transition metals bound to hydroxyapatite [1,16]. The synthesis procedure enables also the hydroxyapatite-based material to have a porous structure with two different lengths of pores scales hierarchy and distinct compositions, which are providing important textural, morphological and structural properties for the solids.

Choosing appropriate amounts of Cu or Co dispersed on hydroxyapatites is one of the contributing factors in obtaining very active catalysts operating under mild temperature and pressure conditions, achieving high conversions and selectivities, preventing coke formation and at the same time improving the lifetime of the catalysts.

## 2. Experimental

### 2.1. Synthesis of the hydroxyapatites

The preparation method of the solids was based on the precipitation of 300 mL of ammonium phosphate,  $(\text{NH}_4)_2\text{HPO}_4$  and 500 mL of calcium chloride,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  solutions, both possessing concentrations of  $0.10 \text{ mol dm}^{-3}$  [12,17]. Initially, the aforesaid ammonium phosphate solution was heated at  $100^\circ\text{C}$ , under reflux for 30 min. Thereafter, the calcium chloride solution was added to the previous ammonium solution together with 25% of ammonium hydroxide solution by heating the mixture at  $100^\circ\text{C}$  and maintaining this temperature for 1 h. Subsequently, a white suspension was formed at  $\text{pH} = 10.5$ , under aging for 24 h. After cooling the system to room temperature, the resultant mixture was filtrated by vacuum and washed until negative tests for chloride ions by considering a filtrated fraction with silver solution. The obtained gel was then

dried in an oven at  $100^\circ\text{C}$  for 24 h and calcined in air at  $550^\circ\text{C}$  for 2 h and the solid was designed as CaHAP.

The copper-containing hydroxyapatites were prepared by using the abovementioned procedure to obtain a (Ca+Cu)/P ratio of 1. Briefly, a 100 mL of ammonium phosphate solution with concentration of  $0.50 \text{ mol dm}^{-3}$  was heated under reflux while stirring. Then, aqueous solutions of calcium chloride and copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), both of them possessing concentration of  $0.10 \text{ mol dm}^{-3}$ , were added dropwise to the previous ammonium solution with vigorous stirring at  $100^\circ\text{C}$ . The pH value of the mixture was controlled at about 10.5 with using a 25% ammonium hydroxide solution. The mixture was strongly stirred at  $100^\circ\text{C}$  and then aged at the room temperature for 24 h. The obtained suspension was filtered and copiously washed with distilled water and the obtained gel was dried and then calcined under air at  $550^\circ\text{C}$  for 2 h. The sample was labelled as CuHAP. Different loadings were obtained by varying the initial copper precursor concentration. For instance, CuHAP4, CuHAP2 and CuHAP1 represent the copper-containing hydroxyapatite possessing Ca/Cu atomic ratios of 4, 2 and 1, respectively.

The Co-containing hydroxyapatites were prepared by adopting the same methodology. The starting materials were  $(\text{Co}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$ ,  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  solutions. In short, a 100 mL of ammonium phosphate solution possessing a concentration of  $0.50 \text{ mol dm}^{-3}$  was refluxed under vigorous stirring. Then, a required amount of equimolar aqueous solutions of calcium chloride and cobalt nitrate solutions was added to the previous solution and the slurry at  $100^\circ\text{C}$  was continued for a further 24 h. After adjusting the pH value to 10.5 with 25% ammonium hydroxide solution and subsequent aging steps, the mixture was filtered off, washed with water, dried and finally calcined under air at  $550^\circ\text{C}$  for 2 h. The sample was synthesized with (Ca+Co)/P ratio of 1 and was designed as CoHAP. Cobalt amounts were varied and samples were labeled as CoHAP4, CoHAP2 and CoHAP1 representing the hydroxyapatites possessing Ca/Co atomic ratios of 4, 2 and 1.

The detailed nomenclature and chemical compositions of the samples are summarized in Table 1.

### 2.2. Characterizations

The determination of the contents of calcium, copper and cobalt was performed by atomic absorption spectroscopy using a GBC 808 AA apparatus. The ultimate elemental analysis of phosphorous was carried out in a Shimadzu MultiSpec-1501 spectrophotometer. Previously, the solids were digested with a mixture of nitric and hydrochloric acids at  $90^\circ\text{C}$  in a sand bath.

X-ray diffraction patterns (XRD) were measured on a Bruker equipment, using the powder method, at  $3^\circ < 2\theta < 75^\circ$  interval.  $\text{CuK}\alpha$  (40 kV, 40 mA) radiation and nickel filter were used for measurements and a step size of  $0.02^\circ$  was applied. The phases were

**Table 1**  
Formulae and contents of calcium (Ca), copper (Cu), phosphorous (P) and cobalt (Co) present on the solids, given in mass (%).

Sample	Formula	Ca (%)	Cu (%)	Co (%)	P (%)
CaHAP	–	29.5	–	–	22.8
CuHAP	$\text{Ca}_{0.95}\text{Cu}_{0.05}\text{HPO}_4$	27.7	2.3	–	22.6
CuHAP4	$\text{Ca}_{0.80}\text{Cu}_{0.20}\text{HPO}_4$	22.8	9.0	–	22.0
CuHAP2	$\text{Ca}_{0.70}\text{Cu}_{0.30}\text{HPO}_4$	19.6	13.3	–	21.6
CuHAP1	$\text{Ca}_{0.60}\text{Cu}_{0.40}\text{HPO}_4$	16.5	17.5	–	21.6
CoHAP	$\text{Ca}_{0.95}\text{Co}_{0.05}\text{HPO}_4$	27.6	–	2.5	21.2
CoHAP4	$\text{Ca}_{0.80}\text{Co}_{0.20}\text{HPO}_4$	22.8	–	8.7	22.0
CoHAP2	$\text{Ca}_{0.70}\text{Co}_{0.30}\text{HPO}_4$	19.4	–	12.5	21.6
CoHAP1	$\text{Ca}_{0.60}\text{Co}_{0.40}\text{HPO}_4$	15.1	–	16.2	20.7

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