



# Possible sites of copper located on hydroxyapatite structure and the identification of active sites for formaldehyde oxidation



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## ABSTRACT

Different methods including ion exchange, co-precipitation and impregnation were used for the preparation of copper doped hydroxyapatite catalysts (CuHAP) to adjust the location of Cu on HAP and resulted in the difference of catalytic performance. Adjustments of synthesis conditions (ion exchange) were adopted for the further identification of active Cu sites for formaldehyde oxidation over CuHAP catalysts. Methods of characterization including XRD, H<sub>2</sub>-TPR, EPR and XPS were used for the identification of Cu species and its environment on the HAP. A hypothesis of five possible sites for Cu location was proposed based on the features of HAP structure and the experimental results. It has also been concluded that the highly-dispersed Cu(II) clusters were mainly responsible for HCHO oxidation. The best activity was achieved over CuHAP (1.4 wt.%) prepared by the ion exchange method with the complete conversion temperature of 180 °C.

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## 1. Introduction

Formaldehyde (HCHO) is one of the most common volatile organic compounds which can be harmful to the health of human beings even exposed under low concentrations. It emits from building and decorating materials, plastic cements, paintings and so forth. Exposure to formaldehyde can cause irritation, wheezing and coughing, fatigue, skin rash and severe allergic reactions at elevated concentrations. Therefore, the removal of HCHO is an issue of great concern that needs to be urgently solved and catalytic oxidation is a promising technique among all the current techniques under investigation [1,2].

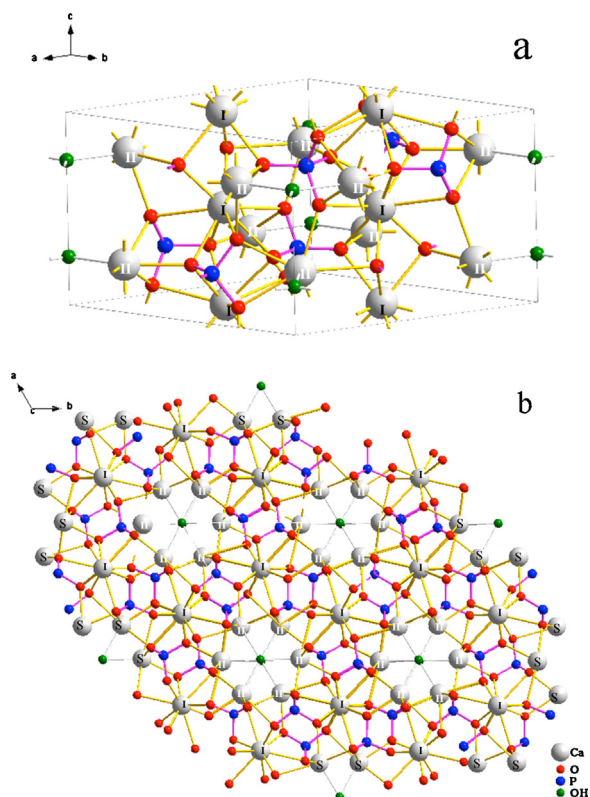
Conventionally, the basic catalytic systems for HCHO oxidation being investigated are noble metal catalysts and transition metal oxides [2–8]. Further modification of the systems, such as mixed transition metal oxides and noble metal doped mixed transition metal oxides are also of great concern because of their potential to improve the catalytic activity [9–11].

Noble metals mainly under investigation are Pt, Au and Ag. The complete conversion temperatures under 100 °C are reported for some of these catalysts [10,12–14]. However, in spite of the relatively effective performance that has been achieved, the high price of noble metal may limit the wide application of these materials.

For the catalytic systems of transition metal oxides, major studied metal oxides are MnO<sub>x</sub>, CeO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> [5,9,11,15–18], the complete conversion temperatures are over 100 °C in most of the cases, even higher than 200 °C under some circumstances. In recently studies, improved catalytic activity has been achieved on transition metal oxides with special structure or the addition of other metals [19–21]. Besides the non-ideal catalytic performance, the toxicity of some transition metal oxides may also hinder the practical application of these materials [22,23]. Therefore, it is necessary to find new materials that are economical, safe and non-toxic to substitute these traditional materials for HCHO oxidation.

Hydroxyapatite, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, is the main inorganic component of natural bone and teeth which means that it is safe and non-toxic. And its flexible and special structure results in the good ion exchange capacity and thermal stability. HAP crystallizes in the hexagonal system (P6<sub>3</sub>/m point group) and has two formula units per unit cell (Fig. 1). Calcium ions at site I (Ca<sub>I</sub>) are coordinated by nine oxygen atoms, while calcium ions at site II (Ca<sub>II</sub>) are coordinated by five oxygen atoms and one hydroxyl group. However, the coordination number of Ca<sub>II</sub> ion is 7, one of them being a weak bond to another oxygen [24]. The main channel of HAP which plays a significant role in the exchange property of HAP is oriented along the c-axis and is delimited by oxygen and six Ca<sub>II</sub> ions. The OH groups hosted by the channels balance the positive charge of the matrix and have great mobility [25–27]. In addition, some Ca<sup>2+</sup> ions (Ca<sub>I</sub> and Ca<sub>II</sub>) exposed on the surface (S) are also easily to be substituted, and these Ca<sub>I</sub> and Ca<sub>II</sub> ions on the surface can be marked as Ca<sub>s</sub>.

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**Fig. 1.** Crystal structure of HAP (I:  $\text{Ca}_I$  II:  $\text{Ca}_{II}$  S:  $\text{Ca}_S$ ): (a) crystal lattice; (b) projection on ((a) and (b)) plane.

HAP has long been used as biological active material and catalyst carriers with a wide application in the fields of biomedical materials and catalysis [28]. Traditionally, as catalytic material, HAP is more often applied and studied for reactions such as Claisen–Schmidt condensation, Michael addition, oxidative dehydrogenation of alkanes, selective oxidation of alcohols and so forth [29–33]. In recent years, HAP has been reported as a promising catalytic material for the reactions of CO oxidation, selective catalytic reduction of  $\text{NO}_x$  and HCHO oxidation [26,28,34–36]. Xu et al. [36] reported the catalytic potential of HAP for HCHO oxidation, and the complete conversion was achieved at 250 °C. Nevertheless, the catalytic performance of pure HAP is still not good enough. In order to achieve the better catalytic activity, other components need to be doped in or loaded on HAP.

Due to the good economical efficiency, as well as the promising catalytic potential, Cu has been used as the main active component of catalysts in various studies [37–41], including the application for HCHO oxidation [6,37,38]. However, the studies of Cu for HCHO oxidation is pretty rare so far, and the catalysts with Cu as the active component do not show satisfactory activity towards HCHO oxidation in the reported works. It is still worthy of detailed study to get deep understanding because it is a promising alternative of noble metals, and further find avenues to improve its performance.

In the present work, HAP was chosen as the catalyst support, and a small amount of copper (Cu), instead of noble metals, was doped in HAP to improve the catalytic activity. Besides the economical efficiency of Cu, Cu doped HAP is also usually used as antibacterial materials because of its environmental safety and stability [42].

Because of the existence of different  $\text{Ca}^{2+}$  sites ( $\text{Ca}_I$ ,  $\text{Ca}_{II}$  and  $\text{Ca}_S$ ) and the skeleton of HAP, there are various sites that are possible for Cu species to locate on. Different locations and species of Cu might lead to the difference in the material structure and composition and further result in the different activity for HCHO oxidation. Therefore, different methods including ion exchange, co-

precipitation and impregnation were used for the preparation of CuHAP to adjust the location of Cu, and the active sites for HCHO oxidation were identified through the adjustment of Cu locations and the portion of certain species. Various characterization techniques, XRD,  $\text{H}_2$ -TPR, XPS and ESR were used to identify Cu species and its environment.

## 2. Experimental methods

### 2.1. Preparation of catalysts

#### 2.1.1. Ion exchange and impregnation methods

The first step for both methods was the preparation of the HAP support. The HAP powder was prepared through an aqueous precipitation method using  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  as precursors. Ammonia ( $\text{NH}_3$ ) solution was used for pH adjustment during the precipitation process. A solution of 0.2 M  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (4.72 g in 100 mL deionized water) was stirred and the temperature was maintained at 40 °C. A solution of 0.3 M  $(\text{NH}_4)_2\text{HPO}_4$  (1.58 g in 40 mL deionized water) was added dropwise to the  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  solution. Then the pH of the suspension was adjusted by ammonia solution (35%) to 10, followed by 8 h of reaction under stirring. After that, the reaction solution was transferred into a Teflon-lined autoclave and heated at 100 °C for 8 h. Finally, the resultant powders were washed and dried at 100 °C overnight and then calcined at 700 °C for 2 h.

As for the ion exchange method, 1 g of HAP powder was introduced into 100 mL 0.01 M copper nitrate (0.242 g  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) solution under stirring. The temperature was maintained at 40 °C during the ion exchange process, which was 2 h. Then the suspension was filtered. After being washed and filtered for several times, the recovered solid was dried at 100 °C for 24 h. The catalyst was marked as CuHAP-IE when different methods were being compared or CuHAP-0.01-1-40 to illustrate the synthesis conditions in detail. Further adjustment of the synthesis conditions included the ion exchange temperature (70 °C), the solution concentration (0.005 M) and the exchange times (2 times). The catalysts obtained were marked as CuHAP-0.01-1-70, CuHAP-0.005-2-40, CuHAP-0.01-2-40.

The impregnated sample was prepared by soaking 1 g HAP powder in 2 mL copper nitrate solution (0.242 g  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) overnight at room temperature. Then the loaded catalyst was dried at 100 °C. The catalyst was marked as CuHAP-IM.

#### 2.1.2. Co-precipitation method

The first step of this method was the preparation of 100 mL solution containing 0.018 mol  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (4.248 g) and 0.002 mol  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.484 g). The remaining steps were as the same as the process preparing HAP powder described above. And the obtained sample was marked as CuHAP-CP.

## 2.2. Characterization techniques

The samples were pre-treated at 400 °C for 1 h in the flow of  $\text{O}_2/\text{Ar}$  before all the characterization tests.

### 2.2.1. XRD

The crystallinity of the catalysts and some Cu species were established and identified by X-ray diffraction (Rigaku D/max- $\gamma\text{B}$  X-ray diffractometer) on operating with a  $\text{Cu-K}\alpha$  radiation in the  $10^\circ \leq 2\theta \leq 80^\circ$  range at RT.

### 2.2.2. BET

Nitrogen adsorption measurements were carried out with a Quantachrom quadrasorb S1. Before analysis, each sample was

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