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Preparation mechanism and catalytic performance of porous copper-doped calcium phosphate material

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ABSTRACT

Through a hydrothermal process, materials contained copper-doped calcium phosphate (copper content 0.04–35.2 wt%) were prepared, which possessed space structure (specific surface area 18.4–89.6 m^2/g) and maintained the activity of copper. The conditions of hydrothermal reaction were optimized, such as adding different organic compounds, adjusting pH, the concentration of reagents, reaction time, and temperature. By employing transmission electron microscope, scanning electron microscope, X-ray diffraction, Fourier transform infrared spectroscopy and other detection methods, to monitor the formation of the material, a mechanism was proposed. The material showed acceptable activity (better conversion than copper phosphate) and good recyclability (more than 5 recycles) in the aerobic oxidation of cyclohexene. The kinetic experiments at different temperature (40–60 °C) and time (0–12 h) indicated the reaction order with respect to cyclohexene was zero.

1. Introduction

Metal phosphate is an important inorganic material, which has been applied in various fields [1–4]. Its rich structural change has significant impact to the study of new materials. For example, in the medical field, calcium hydroxyapatite is used as bone substitute material [5,6]. To improve the drug loading capacity, Wang et al. prepared magnesium substituted β-tricalcium phosphate (β-TCMP) nanospheres with porous structure via self-assembly and transformation process controlled by EDTA ions [7]. In the electrochemical aspect, Bo Pei et al. found that the compound $LiFePO_4$ is a cathode material with good reversibility [8–10]. In the catalyst aspect, metal phosphates were widely used, such as the catalysts for CO oxidation, dehydration of sorbitol under hydrothermal conditions and ketalization of ketones [11–13].

When porous calcium phosphate is used as bone cement, it has excellent biological properties and structural advantages, but with low mechanical intensity [14–16]. It is important to modify the mechanical intensity for better application. Generally, β-TCP cannot form in aqueous solution as the involvement of proton and hydroxyl ions, however, the substitution of magnesium can stabilize β-TCP in the mineralization process [17–21]. We have achieved a good structure by adding magnesium chloride to increase its strength [7]. It gives us the idea to develop a new kind of materials for wider applications, including the catalyst for aerobic oxidation.

Among the catalytic reactions, the oxidation of olefins is an important reaction for converting hydrocarbons into oxygenated compounds, and the oxidation of cyclohexene is always being studied for its industrial application [22–24]. The cyclohexene contains both double bonds and allylic α-H. Epoxy cyclohexane generated from the epoxidation of double bonds, and cyclohexenol and cyclohexenone generated from the oxidation of allylic carbon, are important organic chemicals and intermediates [25,26], which have been widely applied to many fields, such as petroleum, pharmaceuticals, pesticides, feed, polymer materials, food, dyes, textiles, solvents and fine chemical products [27,28]. There are many studies on the oxidation of cyclohexene by using different oxidant agents, for instance, tert-butyl hydroperoxide (TBHP), sodium hypochlorite, hydrogen peroxide, etc [29,30]. The oxidation by using molecular oxygen attracts great attentions, because it is considered as a green oxygen source. However, molecular oxygen is relatively inert; the design of effective catalysts for high conversion and selectivity is still a challenge [31,32].

In this work, we designed and synthesized copper-doped calcium phosphate materials with mesoporous structures. By exploring experimental conditions and detecting different

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Table 1
Add various organic additives to the reaction system at 17 °C and pH = 8–9 for 8 h

Samples ID	Ethanol(mL)	Acetyl acetone (mL)	Na_2EDTA (mmol)
1	0	0	0
2	10	0	0
3	0	0.62	0
4	0	0	2.5
5	0	0.62	2.5

materials, we deduced a reasonable synthesis mechanism. The materials were utilized in the aerobic oxidation of cyclohexene. The conversion and selectivity of the reactants were detected by the gas chromatography (GC), and materials were recycled. We find that there are no significant variations between the materials before and after use, indicating that the material is stable, and it provides a suggestion for the heterogeneous reaction study.

2. Experimental

2.1. Materials

Ethylenediaminetetraacetic acid disodium salt ($Na_2EDTA{\cdot}2H_2O$), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2{\cdot}6H_2O$), copper chloride ($CuCl_2{\cdot}2H_2O$) and tetrasodium pyrophosphate ($Na_4P_2O_7{\cdot}10H_2O$) were analyzed purely. All materials were purchased from Sinopharm Chemical Reagent Co., Ltd., China, and used directly without any further purification. NaOH (1 mol/L) was used for adjusting the pH of the reaction solution. The cyclohexene and benzoate were obtained from Aladdin. Other reagents and solvents were pure analytical grade materials, purchased from commercial sources and used without further purification unless otherwise indicated.

2.2. Materials preparation

In a typical synthesis process, the mixed solution of $Na_2EDTA{\cdot}2H_2O$ (2.5 mmol) and $CaCl_2$ (2.5 mmol) was continually poured into the mixed solution of $Na_4P_2O_7{\cdot}10H_2O$ (1.5 mmol), $MgCl_2{\cdot}6H_2O$ (3.0 mmol) and $CuCl_2{\cdot}2H_2O$ (3.0 mmol) under vigorous stirring. After stirring for 0.5 h, NaOH (1 mol/L) was added into the mixed solution drop by drop until the pH of the mixture was 8, and the hydrosol formed. Then the hydrosol was transferred into a Teflon reactor and heated at 170 °C for 6 h under a static condition. The final product was filtered, washed with distilled water, and dried under vacuum at ambient temperature. In order to study the formation process of the porous catalyst, a series of samples were prepared by varying the preparation conditions, such as different kinds of chelating agents, temperature, reaction time, pH, and $CuCl_2{\cdot}2H_2O$ concentration.

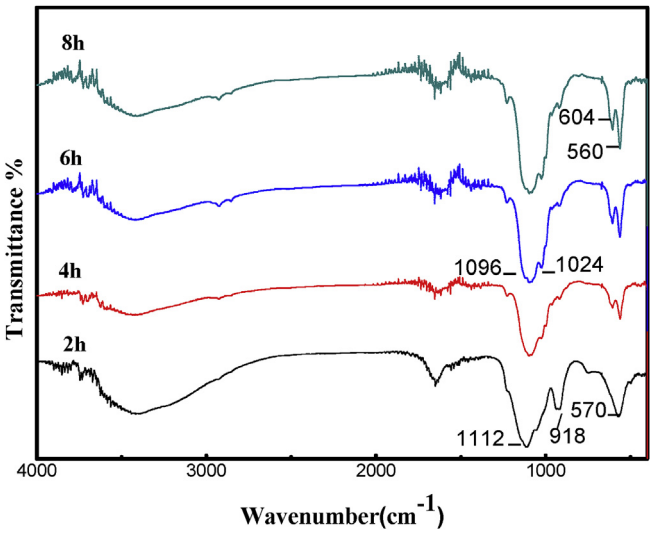

Fig. 2. FT-IR of samples prepared by heating the starting mixtures as sample 4 at 170 °C and pH = 8–9 for different time.

2.3. Oxidation procedure

The oxidation of cyclohexene catalyzed by the as-prepared copper-doped calcium phosphate (CDCP) was performed in a 50 mL one-necked flask at constant temperature under magnetic stirring. Firstly, 10 mmol cyclohexene, 100 mmol chloroform and 20 mg catalyst were added into a flask; then the flask kept vacuum by using the vacuum pump. When the system was heated to 50 °C, molecular oxygen was poured into the mixture from a balloon. The selectivity and conversion were determined by gas chromatography.

2.4. Characterization

The samples for transmission electron microscope (TEM) analysis were dispersed in ethanol by sonication. A small drop of suspension was added into copper mesh and dried in air. TEM analysis was carried out on a JEM-1230 instrument at 80 kV. In order to strengthen conductivity, the samples for scanning electron microscope (SEM) analysis were sprayed with gold. Under the condition of an acceleration voltage of 25.0 kV in Hitachi S-4800 electron microscope, SEM analysis was conducted. The collection of powder

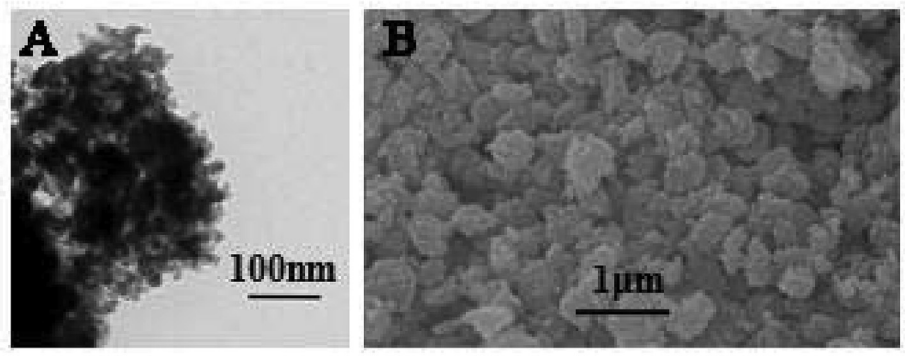

Fig. 1. (a) The TEM image of sample 4. (b) The SEM image of sample 4.