A new way to synthesize benzoin isopropyl ether on Cu-Fe-hydrotalcite

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Abstract

An efficient synthesis of benzoin isopropyl ether with benzaldehyde and propanol in the presence of heterogeneous recyclable Cu-Fe-hydrotalcite catalyst has been explored. Cu-Fe-hydrotalcite was firstly successfully synthesized over Jahn-Teller effect of Cu^{2+}. The catalytic test result showed that Cu-Fe-hydrotalcite could be used as a good catalyst in the synthesis of benzoin isopropyl ether. The highest conversion of benzaldehyde was 59.7% and the selectivity of benzoin isopropyl ether was nearly 100%. By this new method, not only was the cyanide poisoning avoided, but also the synthesis of benzoin isopropyl ether could be completed in one step instead of the traditional two steps with both condensation and etherification.

Key words

benzoin isopropyl ether; benzaldehyde; propanol; Cu-Fe-hydrotalcite

1. Introduction

Benzoin isopropyl ether (also named 2-isopropoxy-2-phenylacetophenone) is of considerable interest in view of their extensive commercial usage as photosensitizers in coatings and printing technologies. Benzoin isopropyl ether is generally synthesized by a two-step process from benzaldehyde and propanol [1]. First, benzaldehyde is catalytically condensed by cyanide in liquid phase to form benzoin. Second, benzoin and propanol are etherified to yield benzoin isopropyl ether in the presence of acid catalysts. The key of the whole process is the synthesis of benzoin. The traditional method involves the use of poisonous cyanide, tedious work up or sensitive catalysts. At the same time, the defects of the catalysts involved in the process greatly limit their application in major industrial processes. Whereas the use of heterogeneous catalysts offers the advantages such as ease of work up, reusability and development of environmentally benign synthetic procedures [2,3]. Therefore, it has been recognized that developing a clean synthetic path of benzoin isopropyl ether is necessary and of significance in green chemistry.

As the strong Jahn-Teller effect of Cu^{2+}, when Cu^{2+} was used to prepare hydrotalcite with trivalent cations by coprecipitation method, Cu^{2+} would form deforming octahedral complex compounds rather than hydrotalcite. Besides, the preparation conditions were very harsh and the crystallinity of the resultant hydrotalcite sample would be very poor [4]. However, catalysts loading copper have wide applications in alkali and redox catalysis. Here, Cu-Fe-hydrotalcite with high crystallinity was successfully prepared by continual coprecipitation method. To our knowledge, there is little information available using continual coprecipitation method to synthesis Cu-Fe-hydrotalcite. At the same time, Cu-Fe-hydrotalcite was firstly used as catalysts for the synthesis of clean benzoin isopropyl ether (Scheme 1). Cu-Fe-hydrotalcite was found to be capable of catalyzing the reaction efficiently, and this environmentally friendly way for the synthesis of benzoin isopropyl ether was explored. The traditional process for the synthesis of benzoin isopropyl ether could be innovated by this new and environmentally benign synthetic technology.
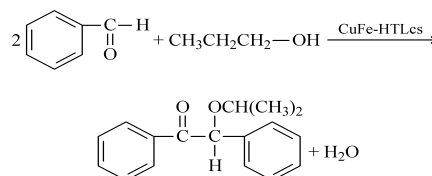
Scheme 1. The formation of benzoin isopropyl ether

2. Experimental

2.1. Preparation and characterization of catalysts

The hydrotalcite containing Cu (II) and Fe (III) was prepared by adding two aqueous solutions simultaneously, one containing copper nitrate (48.32 g, 0.20 mol) and ferric nitrate (40.40 g, 0.10 mol) in deionized water (200 ml) with the required Cu^{2+}/Fe^{3+} ratios and second containing sodium hydroxide (20.00 g, 0.5 mol) in deionized water (500 ml), dropwise into a flask under vigorous stirring at room temperature, while maintaining pH of 4.6 for 0.5 h. Thereafter, sodium carbonate (26.50 g, 0.25 mol) was dripped into the mixture still keeping the pH of 4.6. After being stirred for additional several minutes, the resulting gel-like material was transferred into a Teflon-lined autoclave (100 ml) and aged at 383 K for 0.5 h. After the completion of hydrothermal treatment, the autoclave was cooled down to room temperature naturally and filtered, thoroughly washed with deionized water and dried at 353 K in vacuum oven for 12 h and then further heated in air oven at 423 K for 3 h.

The catalyst was characterized for the crystalline phase(s) and spacing between hydroxide layers by XRD using Rigaku D/max-2500 instrument (40 kV, 100 mA) and Cu K_α ($\lambda = 0.15418$ nm) radiations at a scanning speed of 8º/min, with the scanning range of 5º∼85º.

2.2. Typical procedure for synthesis of benzoin isopropyl ether

Benzoin isopropyl ether was synthesized from benzaldehyde and propanol. A three-neck flask of 250 ml installed condensator and thermometer was fixed in DF-101S compositive magnetic force stirrer, then definite dosage of benzaldehyde, propanol and Cu-Fe-hydrotalcite catalyst (pretreatment under the condition of 423 K with N_2 puffing for 2 h) were added, which the reactant reacted at a constant temperature and routine pressure. The reaction mixture was analyzed by American HP (C6890A/5973MSD) gas chromatography equipped with a DV-101 column (0.2 mm × 0.25 μm × 50 m) and FID detector.

3. Results and discussion

3.1. Catalytic activity of hydrotalcite containing different Cu^{2+}/Fe^{3+} ratios

Three different hydrotalcite samples with different Cu^{2+}/Fe^{3+} ratios were prepared by coprecipitation method [4−6]. Two frequently used techniques are coprecipitation at low and at high supersaturation. In this study we used the latter route for the preparation of hydrotalcites with Cu^{2+} combined with Fe^{3+} in a molar ratio of M^{2+}/M^{3+} ranging from 1.0∼3.0 and NO_3^- was used as charge balancing anion. The structure patterns were recorded by XRD (Figure 1).

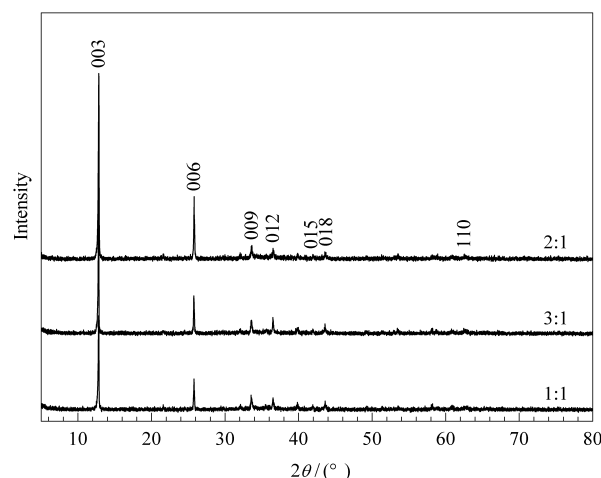**Figure 1.** XRD spectra of Cu-Fe-hydrotalcite samples with different Cu^{2+}/Fe^{3+} ratios

A well-crystallized hydrotalcite structure was presented in all the samples, exhibiting sharp and symmetrical reflections. The crystallinity of the material as evidenced by the sharpness of (003), (006) and (009) reflections indicated that the samples were highly crystalline. The values of the unit cell parameters, with the parameter c corresponding to three times the thickness of the expanded brucite-like layer and the parameter a corresponding to two times of d_{110} decreased with increasing copper content (Table 1). It could be explained by the substitution of Cu^{2+} ions with an ionic radius of 0.69 Å between the layers for smaller Fe^{3+} ion with an ionic radius of 0.64 Å.

Table 1. Crystallographic parameters a and c of different Cu^{2+}/Fe^{3+} hydrotalcites

Samples	Cu^{2+}/Fe^{3+}	a (nm)	c (nm)
1	1.0 : 1.0	0.41546	2.18522
2	2.0 : 1.0	0.41474	2.18079
3	3.0 : 1.0	0.41388	2.17413

Based on the above-mentioned work, Cu-Fe-hydrotalcite was prepared on the proper conditions and applied in the synthesis of benzoin isopropyl ether to study their catalytic performances. Five catalysts with different Cu^{2+}/Fe^{3+} ratios were prepared and their catalytic performance of the conversion of benzaldehyde and selectivity of benzoin isopropyl ether were evaluated. The results obtained are summarized in Table 2.

Table 2. Catalytic performance of different catalysts in the synthesis of benzoin isopropyl ether

Catalyst number	Cu^{2+}/Fe^{3+}	Benzaldehyde conversion (%)	Benzoin isopropyl ether selectivity (%)
0	1.0 : 0.0	26.3	98.8
1	1.0 : 1.0	43.4	99.5
2	2.0 : 1.0	59.7	99.7
3	3.0 : 1.0	51.2	99.4
4	0.0 : 3.0	31.3	99.3

Reaction conditions: the dosage of catalyst, 0.1 g; benzaldehyde, 3 ml; propanol, 50 ml; reaction temperature, 343 K; reaction time, 180 min

Several differences were found in the nature of the catalyst and its catalytic performance. Although the sample without copper had low conversion, as a general trend, benzaldehyde conversion increased with the copper content. The presence of Cu and Fe in the Cu-Fe-hydrotalcite seems to have synergetic effect on the catalytic reaction. The Cu-Fe-hydrotalcite with the molar ratio of $Cu^{2+}/Fe^{3+} = 2.0$ displays the optimally catalytic activity, and the highest conversion of benzaldehyde was 59.7%, while the selectivity of benzoin isopropyl ether was nearly 100%.

3.2. Effect of reaction temperature and time

The effect of reaction temperature on the conversion of benzaldehyde was studied by varying the temperature from 333 K to 353 K as shown in Figure 2, in which the hydrotalcite sample with Cu^{2+}/Fe^{3+} mole ratio of 2.0 : 1.0 was used as a catalyst. Figure 2 reveals that with the increase of reaction time, the conversion of benzaldehyde was gradually increased, however, the selectivity to benzoin isopropyl ether had almost no change, that was nearly 100% from the experiments. The conversion was found to attain its steady state values after running the reaction for 160 min or so. At the same time, the reaction temperature had greatly effect on the conversion of benzaldehyde as shown in Figure 2. The conversion of benzaldehyde was found to increase steadily with the temperature from 333 K to 343 K. When the temperature was increased to 353 K, the conversion of benzaldehyde was slightly reduced. Thus, the proper reaction temperature for synthesis of benzoin isopropyl ether is 343 K.
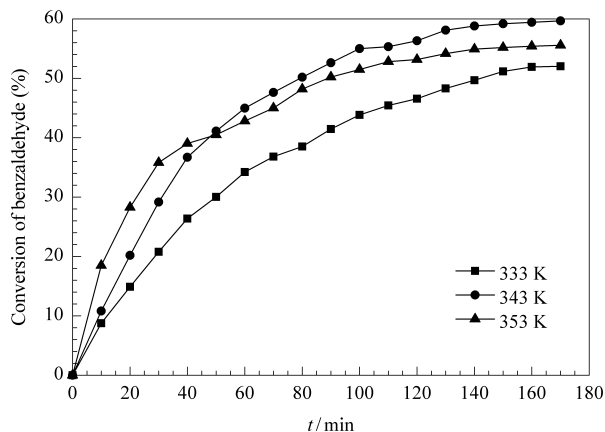

Figure 2. The effect of different temperature and time on the conversion of benzaldehyde

3.3. Durability of hydrotalcite structure during the reaction

Cu-Fe-hydrotalcite was easily separated from the reactant mixture through centrifugal method, and then the catalyst was washed with deionized water and dried at 353 K in an air oven overnight. Figure 3 shows the phases of the catalysts before and after reaction. When the catalyst was reused for

four cycles, the selectivity to benzoin isopropyl ether was still close to 100% in all cases, and the conversion hardly changed with 57.8%.
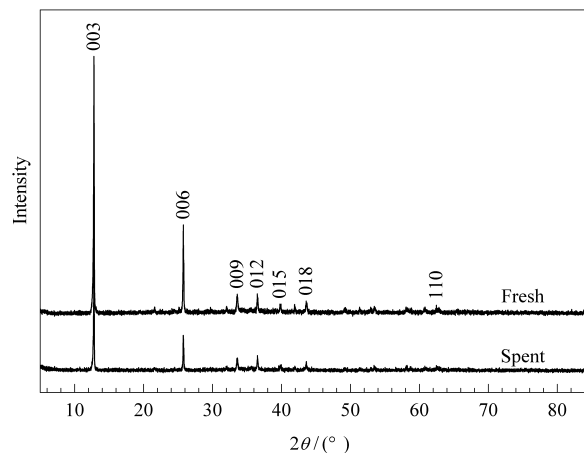

Figure 3. The phases of the catalysts before and after reaction with $Cu^{2+}/Fe^{3+} = 2.0$

3.4. The effect of the structure diversion of catalyst on the reaction

Numerous studies on the physico-chemical properties and thermal stability of various hydrotalcite have been reported [7,8]. It was suggested that upon thermal decomposition, a highly homogeneous mixed oxide is obtained from these materials at about 723 K, which is potentially a basic catalyst for a variety of organic transformations, such as aldol condensation [9], alkylation of phenol [10], epoxidation of limonene [11], oxidative methanol reforming [12] etc. The structures of the catalysts before and after calcination were examined by XRD (Figure 4).
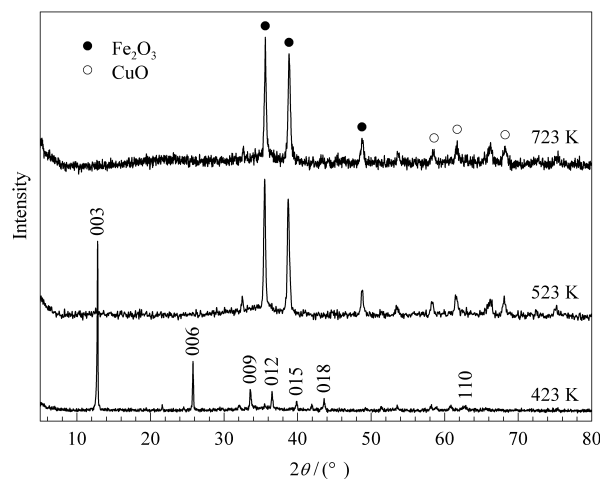

Figure 4. XRD patterns of Cu-Fe-hydrotalcite ($Cu^{2+}/Fe^{3+} = 2.0$) after different calcined temperatures for 3 h

Catalytic activity of complex oxides derived from hydrotalcite was assessed in the synthesis of benzoin isopropyl ether (Table 3).

Table 3. Catalytic performance of Cu-Fe-hydrotalcite after different calcined temperature for 3 h

Calcined temperature (K)	Benzaldehyde conversion (%)	Benzoin isopropyl ether selectivity (%)
423	59.7	99.7
523	43.6	99.7
623	25.2	98.7
723	14.6	98.4
823	0.0	0.0

Reaction conditions were same as those in Table 2

Table 3 presents the effect of the structure of Cu-Fe-hydrotalcite on the reaction. The structure of the catalyst had substantial diversion after calcination comparing to the fresh catalyst. The layered structure of Cu-Fe-hydrotalcite catalyst was destroyed to form complex oxides after calcinations at a temperature as high as 823 K (Figure 4), and the formed complex oxides have no activity at all fit for the reaction (Table 3). Comparing the catalysts calcined at a temperature ranging from 423 K to 523 K, the conversion of benzaldehyde sharply reduced from 59.7% to 43.6%. These results indicated that the layered structure of Cu-Fe-hydrotalcite is favorable for the reaction. Moreover, if the calcined temperature increasing from 623 K to 823 K, the conversion of benzaldehyde gradually reduced from 25.2% to 0.0%. This implies that all layered structure of Cu-Fe-hydrotalcite is destroyed and the formed mixed metal oxides are heavily sintered.

4. Conclusions

An efficient useful and greener method has been developed for the synthesis of benzoin isopropyl ether with benzaldehyde and propanol. In comparison with the reported traditional method by using of poisonous and expensive catalysts, this suggested process employs a layered structure of Cu-Fe-hydrotalcite as a heterogenous catalyst under mild reaction conditions, which is easily removed from the product and can be recycled for several times. The catalyst with a layered structure of Cu-Fe-hydrotalcite in molar ratio of $Cu^{2+}/Fe^{3+} = 2.0$ shows a high conversion of 59.7%, and the selectivity for benzoin isopropyl ether with nearly 100%. The layered structure and synergetic effect of copper and ferric play a crucial role for the catalytic synthesis of benzoin isopropyl ether.

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