Recyclable CuMgAl hydrotalcite for oxidative esterification of aldehydes with alkylbenzenes

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ABSTRACT

A series of hydrotalcite-like compounds with various Cu:Mg:Al molar ratios were prepared by the co-precipitation method. The catalytic performance for oxidative esterification of aldehydes was investigated. X-ray diffraction, N₂ adsorption–desorption (BET), hydrogen temperature-programmed reduction (H₂-TPR), X-ray photoelectron spectroscopy, the scanning electron microscope (SEM), the transmission electron microscope and atomic absorption spectrometry were used to characterize the catalysts. The results showed that the benzyl benzoate product was obtained in good to excellent yield using tert-butyl peroxybenzoate as oxidant at 90°C under air atmosphere over Cu₂Mg₁Al₁-LDH catalyst. The catalyst can be recovered and used with 45% conversion after recycling five times. The oxidative esterification reaction in the heterogeneous system is environmentally friendly.

The Cu₂Mg₁Al₁-LDH catalyst prepared by co-precipitation method showed high catalytic activity for oxidative esterification of aldehydes. 81.0% yield of benzyl benzoate with benzaldehyde and toluene as reactants was obtained using tert-butyl peroxybenzoate as oxidant at 90°C under air atmosphere over Cu₂Mg₁Al₁-LDH catalyst. The catalyst can be recovered and used with 45% conversion after recycling five runs. The oxidative esterification reaction in the heterogeneous system is environmentally friendly.

1. Introduction

Currently, carboxylic esters are widely used in the fields of materials, pharmaceuticals, perfumes, coatings and cosmetics. The traditional synthetic method for carboxylic ester synthesis is used for esterification reactions between carboxylic acids or their derivatives (including acyl chlorides and anhydrides) and alcohols. However, this method has numerous drawbacks, including a complicated procedure, high reaction temperature, strong acidic conditions, limited substrates and unwanted by-products (1–5). A cross-dehydrogenation coupling method involving activation of the C–H bond is
thought to be an efficient procedure to synthesis aromatic esters due to high atom economy and lack of necessity to activate the substrate. In this protocol, the most often used catalysts are transition metal complexes, such as copper complexes. And organic ligands and additives are necessary for the reaction system. Saroj group used copper salts catalyzed methodology with alkylbenzenes and aldehydes as precursors for the synthesis of benzylic esters via a CDC approach, in which hydrated copper (II) acetate provided a superior yield to other Cu salts. The pioneering work of direct functionality at the relatively nonactivated alkylbenzenes has rarely been realized (6). However, due to the fact that it is difficult to recycle the catalysts, the organic ligands used are harmful to the environment and purification of the product is difficult because of the complicated reaction systems (7), the use of homogeneous catalytic systems in many fields is still hindered. With this motivation, to develop heterogeneous catalysts for oxidative esterification may be a cost-effective and efficient method from a “green chemistry” perspective.

Hydrotalcite compounds are layered double hydroxides that are composed of positively charged two-dimensional brucite layers with anionic species such as hydroxide and carbonate located in the interlayers. Hydrotalcite compounds have unusual physical-chemical properties due to their unique layered structure, including high thermal stability, tunable components, acidic-basic properties and structure memory effects (8). Based on these properties, hydrotalcite compounds have been widely used in the field of catalysis, particularly in organic synthesis, in recent years (9–11). Compared with the homogeneous system, hydrotalcite compounds in the heterogeneous system are easy to separate and reuse, and therefore have good prospects for the application. In this paper, we initiate the investigation by reacting toluene with benzaldehyde in the presence of CuMgAl hydrotalcite catalyst. A series of hydrotalcite-like compounds containing copper were prepared, and the effects of these catalysts were studied in oxidative esterification for the synthesis of the carboxylic ester from toluene and benzaldehyde.

2. Experimental

2.1. Catalyst preparation

The CuMgAl hydrotalcite-like catalysts were prepared by the co-precipitation method (12). As an example, Cu2Mg3Al1-LDH was prepared using the following procedure: a mixture of 200 mL metallic salt solution containing Cu(NO3)2·3H2O (14.4960 g), Mg(NO3)2·6H2O (7.6920 g) and Al(NO3)3·9H2O (11.2539 g), with a molar ratio Cu:Mg:Al of 2:1:1. The metallic salt solution and 100 mL NaOH solution (4 mol/L) were added dropwise into a flask containing 100 mL Na2CO3 solution (0.5 mol/L) at a pH of 9.0–10.0 under magnetic stirring. After 0.5 h aging, the mixture was separated. The resulting light grey-blue solid was washed with deionized water several times until neutral, then dried in an oven at 70°C for 24 h.

A series of CuMg3Al1-LDH hydrotalcites-like compounds with different Cu:Mg:Al molar ratios, including Cu1Mg3Al1-LDH, Cu1.5Mg1.5Al1-LDH and Cu3Al1-LDH, were prepared by this method.

2.2. Catalyst characterization

The scanning electron microscope (SEM) was run on a Hitachi SU-8010 and morphological analysis was carried out setting the acceleration voltages between 1.00 and 10 kV without significant differences. Transmission electron microscope (TEM) images were recorded using a JEOL JEM-1210 microscope with accelerating voltage of 200 kV. The samples were prepared by a suspension method. X-ray diffraction (XRD) patterns of the samples were obtained using a Regaku Ultima IV system with graphite monochromatized Cu–K radiation at 5° to 80° 2θ degrees. The specific surface area was calculated using the BET method on an ASAP 2020 instrument (Micromeritics Instrument Corp.). Samples were outgassed at 100°C for 3 h before measurement and measured by static nitrogen adsorption at 196°C. Hydrogen temperature-programmed reduction (H2-TPR) analysis was carried out using a TPR/TPD Chemisorption Analyzer. 50 mg samples were placed in a quartz tube and filled with mixing gas H2+Ar (VH2 = 5%) with the temperature increasing from room temperature to 800°C at a rate of 10°C/min. Hydrogen consumption was analyzed by TCD detector. The composition of the sample was estimated by atomic absorption spectroscopy (AAS) on a TAS-990 Atomic Absorption Spectrometer. The parameters for measurements were: wavelength from 200 to 900 nm and a detection limit of 1 mg/L.

2.3. Evaluation of catalytic performance

The reaction was conducted in a quartz tube with a magnetic stirrer. Oxidative esterification to synthesis a carboxylic ester, with toluene and benzaldehyde as reactants, was used as the model reaction. The catalyst (25 mg), alkylbenzene (2 mL), tert-butyl peroxbenzoate (TBPB) (0.5 mmol) and aldehyde (0.2 mmol) were added to the test tube. The solution was heated to 90°C for 24 h with magnetic stirring. After cooling to room temperature, the sample was centrifuged and the precipitate was filtered. The components of solution were analyzed by GC-MS.
(Shimadzu GC-2014) with FID detector and an HP-5 capillary column (50 m length, 0.25 mm internal diameter and 0.25 μm film thickness). The products were identified by comparison with known standard samples.

The recyclability of the catalyst was investigated. After each reaction cycle, the solvent, substrate and products were removed by centrifugation. The separated catalyst was washed thoroughly twice with distilled water and twice with ethanol followed by centrifugal separation and drying at 80°C for 10 h. The resultant sample was reused.

3. Results and discussion

3.1. Results of catalyst characterization

3.1.1. X-ray diffraction

Figure 1 shows the XRD patterns of Cu$_x$Mg$_{3-x}$Al$_1$-LDH. Broad peaks around at 11.6°, 23.4°, 34.8° and 60.5° observed were assigned to (003), (006), (009) and (110) planes, that are characteristic peaks of hydrotalcite-like compounds, respectively (13). Especially, the diffraction peaks of the (003), (006) and (009) planes, they can determine whether the hydrotalcite compounds have layered structures. Furthermore, the interlayer space of hydrotalcite, $d_{003}$, is dependent on both the anion radius between the layers and its interaction with cations on the hydrotalcite layer. With an increase in Cu$_2^+$ content, the positions of the characteristic peaks of Cu$_x$Mg$_{3-x}$Al$_1$-LDH did not change significantly, as a result of the similar ion radius of Mg$_{2+}$ ($r = 0.072$ nm) and Cu$_{2+}$ ($r = 0.073$ nm). Wherein, the intensity of the characteristic peaks strengthened gradually with increasing Cu$_{2+}$. However, when Mg$_{2+}$ was completely replaced by Cu$_{2+}$, the intensity became relatively weak for the diffraction peaks of (009) and (110), while relatively strong for the diffraction peak of (003) (14). Additionally, the characteristic peak of CuO appeared at 35.5°, which may be related with the Jahn–Teller effect of Cu$_{2+}$, causing the layer space to increase and the partial structure of the hydrotalcite-like compound to collapse (12). It was worth to note that the hydrotalcite structure of Cu$_2$Mg$_1$Al$_1$-LDH has been completely destroyed after five runs in the reaction.

3.1.2. N$_2$ physical adsorption–desorption

The specific surface area of Cu$_1$Mg$_2$Al$_1$-LDH, Cu$_{1.5}$Mg$_{1.5}$Al$_1$-LDH, Cu$_2$Mg$_1$Al$_1$-LDH and Cu$_3$Al$_1$-LDH hydrotalcite-like compounds was 109, 86, 92.5 and 18.9 m$^2$ g$^{-1}$, respectively. It could be found that with increasing Cu$_{2+}$ amount in the catalyst, the surface area of the sample decreased. The low surface area of Cu$_3$Al$_1$-LDH might be related to the collapse of the LDH structure, which is consistent with the XRD characterization result.

3.1.3. H$_2$-TPR

Figure 2 shows the H$_2$-TPR profiles of Cu$_x$Mg$_{3-x}$Al$_1$-LDH. The peaks in the range of 250–400°C were ascribed to the reduction of Cu$_{2+}$ to Cu (15). For the Cu$_1$Mg$_2$Al$_1$-LDH catalyst, only one reduction peak was observed, implying the good dispersion of Cu$_{2+}$. Other catalysts had two reduction peaks: one at a lower temperature, relating to the reduction of highly dispersed Cu$_{2+}$ on the surface, and the other at a higher temperature relating to the reduction of Cu$_{2+}$ in the bulk of catalyst (16). With an increase of Cu$_{2+}$, the reduction peak of highly dispersed Cu$_{2+}$ shifted to a lower temperature, suggesting an easier reduction of Cu$_{2+}$. Our result is consistent with previous research (17). However, the reduction peak of the Cu$_3$Al$_1$-LDH catalyst shifted to a higher temperature, due to the occurrence of CuO. In addition, as the Cu$_{2+}$ content increased, the area of the
reduction peak increased gradually, suggesting that H₂ consumption increased gradually.

3.1.4. Results of XPS characterization

To illustrate the valence of the active species, the X-ray photoelectron spectroscopy (XPS) analysis technique was used to characterize Cu₂Mg₁Al₁-LDH. Figure 3 shows that the peak of Cu 2p₃/₂ was in the range of 933~937 eV, demonstrating that the copper species exist as Cu²⁺ in both the fresh and recycled catalysts (18). The satellite peaks with binding energies of 940~945 eV, further confirm the presence of Cu²⁺ (19), consistent with the results of H₂-TPR.

Figure 3. Cu 2p XPS profiles of Cu₂Mg₁Al₁-LDH catalyst: (a) fresh catalyst; (b) recycled catalyst.

3.1.5. SEM and TEM

SEM and TEM images can give detailed information about the shape and the morphology of the materials (Figure 4). From the SEM micrograph, it can be seen that the catalyst consists of thin platelets, suggesting the formation of layered structure. From the TEM micrograph, some lamellar platelets and folded plates can also be observed.

Figure 4. SEM and TEM of Cu₂Mg₁Al₁-LDH catalyst.

Table 1. The effect of temperature on catalytic performance.

| Temperature (°C) | Conv (%) | Y (%) |
|-----------------|----------|-------|
| 80              | 73.1     | 53.7  |
| 90              | 94.7     | 81.0  |
| 100             | 76.0     | 59.2  |

Notes: Reaction conditions: benzaldehyde (0.2 mmol), toluene (2 mL), oxidant (0.5 mmol). Catalyst: Cu₂Mg₁Al₁-LDH (25 mg), 24 h.

Table 2. The influence of various oxidants for synthesis of benzyl benzoate.

| Oxidant                     | Conv (%) | Y (%) |
|-----------------------------|----------|-------|
| –                           | 0        | 0     |
| Tert-butyl peroxybenzoate   | 94.7     | 81.0  |
| Tert-butyl hydroperoxide    | 58.7     | 9.2   |
| Cumene hydroperoxide        | 34.1     | 16.8  |
| Peracetic acid              | 58.7     | 0     |
| Di-tert-butyl peroxide      | 61.8     | 6.9   |
| Benzoyl peroxide            | 26.5     | 16.8  |

Notes: Reaction conditions: benzaldehyde (0.2 mmol), toluene (2 mL), oxidant (0.5 mmol). Catalyst: Cu₂Mg₁Al₁-LDH (25 mg), 90°C, 24 h.

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Notes: Reaction conditions: benzaldehyde (0.2 mmol), toluene (2 mL), oxidant (0.5 mmol). Catalyst: Cu₂Mg₁Al₁-LDH (25 mg), 90°C, 24 h.
3.1.6. Results of AAS characterization

The Cu$^{2+}$ content of the Cu$_2$Mg$_1$Al$_1$-LDH catalyst was determined by AAS. The Cu$^{2+}$ content decreased from 6.4% to 5.3% after five recycles, suggesting partial Cu$^{2+}$ leaching during the reaction.

3.2. Results of catalytic performance

3.2.1. Optimization of the reaction conditions

The effect of temperature on catalytic performance for the synthesis of benzyl benzoate was investigated. Table 1 shows the yield could reach 81% with TBPP as oxidant under the optimal temperature of 90°C, which is comparable with the results in the literature (6). In the control experiments carried out with either copper catalyst or TBHP alone, no desired product was detected.

The influence of oxidants on the synthesis of benzyl benzoate was studied. Table 2 shows that the esterification reaction could not be carried out without oxidants. The use of tert-butyl peroxybenzoate (TBPB) as the oxidant could afford the highest yield of benzyl benzoate.

3.2.2. The effect of Cu$^{2+}$ content on performance for the synthesis of benzyl benzoate

To study the effect of Cu$^{2+}$ content on the performance, the catalytic performance of Cu$_x$M$_{3-x}$A$_1$-LDH hydrotalcite-like compounds containing various amounts of Cu$^{2+}$ was examined for the synthesis of benzyl benzoate from toluene and benzaldehyde. Table 3 demonstrates that Mg$_3$A$_1$-LDH had no catalytic activity. However, with the introduction of Cu$^{2+}$, benzyl benzoate was obtained at a 70.2% yield, showing that Cu$^{2+}$ was the active species. With a further increase in copper content, the yield of benzyl benzoate increased gradually. The highest yield was obtained when the ratio of Cu:Mg was 2, which may be related to the high specific

| Catalysts | Conv$^a$ (%) | Yb$^b$ (%) |
|-----------|-------------|------------|
| Mg$_3$A$_1$-LDH | 0 | 0 |
| Cu$_1$M$_2$A$_1$-LDH | 78.8 | 70.2 |
| Cu$_2$M$_1$A$_1$-LDH | 80.8 | 73.0 |
| Cu$_3$A$_1$-LDH | 94.7 | 81.0 |
| Cu$_4$A$_1$-LDH | 64.9 | 37.7 |

Note: Reaction conditions: benzaldehyde (0.2 mmol), toluene (2 mL), oxidant (0.5 mmol), catalyst (25 mg), 90°C, 24 h. 
$^a$Conversion of benzaldehyde. 
$^b$Yield of benzyl benzoate.

3.1.6. Results of AAS characterization

The Cu$^{2+}$ content of the Cu$_2$Mg$_1$Al$_1$-LDH catalyst was determined by AAS. The Cu$^{2+}$ content decreased from 6.4% to 5.3% after five recycles, suggesting partial Cu$^{2+}$ leaching during the reaction.

| No | Reactant 1 | Reactant 2 | Product | Yield (%) |
|----|------------|------------|---------|-----------|
| 1  |            |            | ![Product 1](image1) | 59.1      |
| 2  |            | ![Reactant 2](image2) | ![Product 2](image3) | 57.0      |
| 3  | ![Reactant 3](image4) | ![Reactant 2](image2) | ![Product 3](image5) | 8.2       |
| 4  | ![Reactant 4](image6) | ![Reactant 2](image2) | ![Product 4](image7) | 13.5      |
| 5  | ![Reactant 5](image8) | ![Reactant 2](image2) | ![Product 5](image9) | 16.6      |

Note: Reaction conditions: benzaldehyde or derivative (0.2 mmol), toluene or derivative (2 mL), oxidant (0.5 mmol), catalyst (25 mg), 90°C, 24 h.
surface area of Cu$_2$Mg$_1$Al$_1$-LDH. When Cu$^{2+}$ completely replaced Mg$^{2+}$, the yield of product over Cu$_3$Al$_1$-LDH declined dramatically, which might be resulted from the partial collapse of the hydrotalcite structure, decrease in the surface area as well as the formation of CuO. Furthermore, Table 4 shows the influence of Cu$_2$Mg$_1$Al$_1$-LDH dosage for the synthesis of benzyl benzoate. 25 mg catalysts in the system gave the best performance.

3.2.3. The synthesis of an ester from various substrates

The scope of the method for oxidative esterification was investigated using a variety of aldehydes and toluene and their derivatives under the optimized reaction conditions in Table 5. P-xylene and m-xylene reacted with benzaldehyde with product yields of 59.1% and 57%, respectively. However, with the introduction of either electron-donating or electron-withdrawing groups over the benzaldehyde reactant, the product yields were relatively low, which might be related steric hindrance.

3.2.4. Reusability of the catalyst

The reusability of the catalyst is of importance and is one of the main advantages of a heterogeneous catalyst in consideration of the industrial application. The reusability of Cu$_2$Mg$_1$Al$_1$-LDH was studied and we found that the catalyst could be readily recovered and reused. Figure 5 shows that the product yields changed from 81.0% to 44.9% after five runs, probably relating to the partial leaching of Cu$^{2+}$ as confirmed by AAS and the disappearance of hydrotalcite structure proved by the XRD.

4. Conclusion

In summary, benzyl benzoate synthesis from benzaldehyde and toluene was achieved over hydrotalcite-like compounds containing Cu$^{2+}$. Cu$_2$Mg$_1$Al$_1$-LDH showed the highest catalytic performance with 94.7% conversion of benzaldehyde and 81% yield of benzyl benzoate due to its high specific surface area and well dispersed Cu$^{2+}$ active species. The solid catalyst was recovered and reused, illustrating that this new heterogeneous catalytic systems could be cost-effective and environmentally friendly. The catalytic performance over the Cu$_2$Mg$_1$Al$_1$-LDH catalyst decreased from 81% to 45% after five runs, relating to the leaching of the partially active Cu$^{2+}$ species and the disappearance of hydrotalcite structure.

Disclosure statement

No potential conflict of interest was reported by the authors.

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