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Facile synthesis of eco-friendly Cu-hydrotalcite catalysts for highly selective synthesis of furfural diethyl acetal and benzoin ethyl ether

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ABSTRACT

A series of eco-friendly Cu-hydrotalcite (HT) catalysts (Cu-Fe, Cu-Al, Cu-Cr) were facilely and successfully synthesized by a modified co-precipitation method. The as-prepared Cu-hydrotalcite catalysts were highly selective for the synthesis of value-added furfural diethyl acetal and benzoin ethyl ether, whereas furfural diethyl acetal (97.5% selectivity at 49.3% conversion of furfural) and benzoin ethyl ether (98.4% selectivity at 43.7% conversion of benzaldehyde) were highly selectively produced on the Cu-Fe hydrotalcite catalyst, respectively. The eco-friendly Cu-hydrotalcite catalysts were easy to be recycled and maintained high stability, which may be a good candidate for the general application in the reaction of aldehyde and ethanol.

Keywords: Synthesis; Cu-hydrotalcite; high selectivity; furfural diethyl acetal; benzoin ethyl ether.

Kai Yan started his Ph.D. study in Max-Planck-Institute for Coal Research in 2008 and obtained his PhD degree from RWTH Aachen University in 2011. Currently, he is working on the synthesis of novel mesoporous supported nanomaterials and the design of green alternative for catalytic conversion of biomass-derived monomers into biofuels and other value-added products. He has published 20 peer-reviewed journal articles and filed two patents.

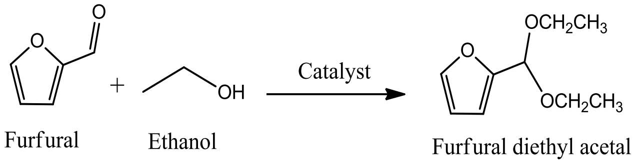
Xianmei Xie received her Ph.D. from Taiyuan University of Technology. Since 2001, she became a Full Professor in Taiyuan University of Technology. In 2003, she was awarded "The First Outstanding Teaching Award" in Shanxi. In 2006, she won the 2nd Place of "Development of Scientific Technology Award" in Shanxi. In 2006 and 2008, she won the 2nd Place of "The Best Teaching Award", respectively. From 2003 to 2012, she worked as the Editor of the following books titled "Physical Chemistry", "Basic Chemistry Experiments in College", and "Guide to Learn Physical Chemistry". Her group has published more than 20 peer-reviewed international journal articles and filed three patents. Her group research interests span the areas of Inorganic Microporous Materials, Green Chemistry, Nanotechnology and Heterogeneous Catalysis.

Introduction

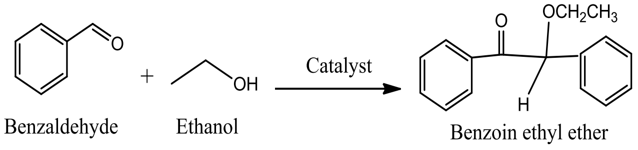
Catalytic conversion of biomass-derived products has received a great deal of attention in the last decades, which is an alternative route for the sustainable production of value-added chemicals and biofuels **[1-3]**. Furfural, which is often produced by the hydrolysis or dehydration of xylan contained in lignocelluloses **[4,5]**, is recently considered as a new building block to yield a broad range of versatile chemical structure. This is due to its two functional groups, an aldehyde (C=O) and a conjugated system (C=C-C=C), making furfural as a versatile building block for the synthesis of several important organic chemicals such as furfural diethyl acetal, furfuryl alcohol, 2-methylfuran etc **[6-9]**.

Furfural diethyl acetal is among the most important perfume materials and also industrial solvent for organic synthesis **[10]**. The synthesis of furfural diethyl acetal from furfural with bioethanol (**Scheme 1**), occurs even at room temperature, but the reaction is very slow and needs to be accelerated either by using high temperature or by using a catalyst to achieve the equilibrium conversion in a reasonable period of time **[11]**. In the last a few decades, different catalysts have been developed for the synthesis of acetals. The mineral acid (e.g. H_2SO_4, conventionally used as catalyst in factories) often present good activities **[12]**. However, they often induced several problems, such as the erosion of equipment, difficult recycle of the catalyst and generation of significant waste with low quality of the products. Due to its easy recycle and separation, heterogeneous catalysts become more attractive in practice. Besides, the solid catalysts are easier to be separated and there is no need for neutralization, can be used for several times, and are less corrosive than mineral acid. Heterogeneous acid catalyst based on heteropoly acids (HPAs) has recently developed for the synthesis of acetals, where the HPAs provide strong Brönsted acidity, have potential economic and green benefits **[13]**. However, HPAs are readily soluble in many organic solvents (e.g. ethanol), which results in a difficult separation from the reaction mixture. Recently, we found the resulted Cu-Al hydrotalcite that was prepared by a co-precipitation method with a constant pH-value, which was good for the synthesis of furfural diethyl acetal **[14]**. However, the efficient synthesis of furfural diethyl acetal is still largely lacked.

Benzoin ethyl ether, synthesized from benzaldehyde and bioethanol (**Scheme 2**), is often employed as an important value-added chemical for the photosensitive plastic and UV-curing coatings **[15, 16]**. The traditional two steps synthesis of benzoin ethyl ether is often achieved using the homogeneous toxic cyanide catalyst (e.g. KCN) and enzyme (e.g. fungi) **[17, 18]**. Recently, our previous studies show that a Ni-Al-Ce HT catalyst and a composite of HT with zeolite ZSM-5 catalyst was good for the synthesis of benzoin ethyl ether **[19, 20]**. However, the composite used for synthesis of benzoin ethyl ether was easy to aggregate and even partial leach during the aqueous reaction. An efficient and environmental benign manner to synthesize benzoin ethyl ether is still largely unexplored.



Scheme 1. Synthesis of furfural diethyl acetal from furfural and ethanol.



Scheme 2. Synthesis of benzoin ethyl ether from benzaldehyde and ethanol.

Herein, we report a series of low-cost Cu-hydrotalcite catalysts (Cu-Fe HT, Cu-Al HT, Cu-Cr HT) synthesized by a modified co-precipitation method under a variable pH value, which are highly selective for the synthesis of value-added furfural diethyl acetal (**Scheme 1**) and benzoin ethyl ether (**Scheme 2**), respectively. The synthesized Cu-hydrotalcite catalysts are non-corrosive and environmentally friendly, display easy recycle and separation, present fewer disposal problems. The Cu-hydrotalcite catalysts developed in this work may be a good candidate for the general application in the reactions of aldehyde and bioethanol.

Experimental

Chemicals

All the following chemicals were purchased from the chemical companies and directly used without any purification. Anhydrous ethanol (AR, 99.8%), furfural (AR), NaOH (AR, ≥97.0%), benzaldehyde (AR, 98%), $Cu(NO_3)_2 \cdot 6H_2O$ (AR), $Cr(NO_3)_3 \cdot 9H_2O$ (AR), $Fe(NO_3)_3 \cdot 9H_2O$ (AR) and $Al(NO_3)_3 \cdot 9H_2O$ (AR) were bought from Tianjing Kemiou Company.

Hydrotalcite synthesis

Cu-hydrotalcite catalysts were facilely synthesized by a modified co-precipitation method under a variable pH value using NaOH as a precipitation agent **[21,22]**, which involves the hydrotalcite crystal formation and the crystal growth. The typical procedure for the synthesis was as following: The pre-calculated volume of $Cu(NO_3)_2 \cdot 6H_2O$ (1 M) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.5 M) or $Al(NO_3)_3 \cdot 9H_2O$ (0.5 M) or $Cr(NO_3)_3 \cdot 9H_2O$ (0.5 M) based on the Cu^{2+}/Fe^{3+} (Al^{3+}, Cr^{3+}) ratio of 2 was fully mixed into a 250 mL beaker, then NaOH solution (1 M) was added into the former solution at the speed of 1 drop/second under the stirring condition. When the final pH of the reaction mixture reached ~4.9, the addition of NaOH solution was stopped and the solution was continue to be stirred for another 0.5 h. The resulting slurry was under hydrothermal treatment at 110 °C for 6 h. The precipitate was then filtered, washed well with deionized water for three times and dried at 110 °C for 24 h.

Catalyst characterization

The powder X-ray diffraction (XRD) patterns for qualitative phase analysis were collected on a Rigaku D/Max2500 in transmission geometry with a primary monochromator and a linear position sensitive detector, with $CuK\alpha_1$: 1.5418 Å as a radiation source. The data were collected in the range of 5-75^o with a step width of 8^o (2θ).

Elemental chemical analysis for Cu, Al and Cr was carried out with inductively coupled plasma (ICP) spectrometry (Australian Labtam Co. Labtam8410). Samples were dried at 100 ^{o}C for 24 h prior to analysis, and solutions were prepared by dissolving the samples in dilute hydrochloric acid (1:1). The rate of cooling gas is 10.5 L/min and the flue rate of carrier gas is 1.0 L/min.

The Fourier transform infrared spectrums (Nicolet 6700 FTIR) of the sample were recorded in the range of 400 ~ 4000 cm^{-1} with a resolution of 2 cm^{-1}. The samples were pressed in KBr pellets. Spectroscopic manipulation such as baseline adjustment, smoothing and normalization were performed using Spectracalc software. Thermo gravimetric analysis (TG) and Differential thermal analysis (DTA) were performed on WCT-2 differential thermal balance using flowing N_2. Samples were dried at 100 ^{o}C for 24 h prior to analysis and ~10 mg samples were heated at a heating rate of 10 ^{o}C/min up to 600 ^{o}C. Transmission electron microscopy (TEM) was used to investigate textural features of the Cu-hydrotalcite catalysts with a JEOL 2010 instrument.

Catalytic synthesis of furfural diethyl acetal

The synthesis of furfural diethyl acetal was performed in a 50 mL three-neck flask with a flux condenser and thermometer under argon environment. In a typical reaction procedure, the pre-calculated amounts of furfural (3 mL) with ethanol (40 mL) were transferred into the flask. To the solution, catalyst (105 mg) was added. The flask was then transferred into the pre-heated water bath, which took ~10 min to reach the desired temperature. Zero time was taken to be when the temperature reached the desired temperature of 70 ^{o}C. The reaction products were separated with the used catalysts after reaction time of 1.5 h through centrifugation for 20 min. The obtained solution was filtrated by neutral aluminium oxide and then analyzed by HP (C6890A) gas chromatography equipped with a DV-101 column (0.2 mm × 0.25 μm × 50 m) and FID detector. The injected volume was 0.2 μL. The external method was used to analysis. The corresponding conversion, selectivity and yield were calculated based on GC analysis results**.**

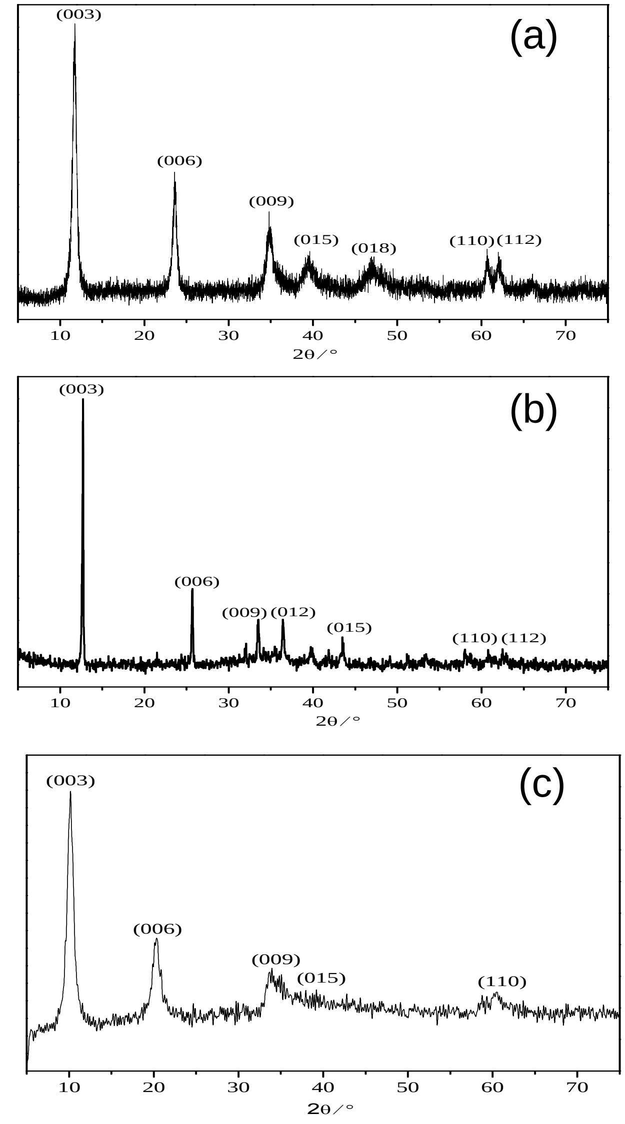


Fig. 1. X-ray patterns of the synthesized Cu-Al HT (A), Cu-Fe HT (B), Cu-Cr HT (C).

Catalytic synthesis of benzoin ethyl ether

One-pot synthesis of benzoin ethyl ether was performed in a 50 mL three-necked flask with a flux condenser and thermometer under an argon environment. In a typical reaction procedure: firstly, benzaldehyde (3 mL) and ethanol (40 mL) was transferred into the flask. Secondly, the catalyst (104 mg) was added to the solution, followed by the filling and releasing of argon three times. Thirdly, the flask was transferred into the pre-heated water bath, which took ~10 min to attain the desired temperature. Zero time was taken to be when the temperature reached the desired temperature. Finally, the reaction products were separated from the used catalysts through centrifugation for 10 min. The obtained solution was filtrated by neutral aluminium oxide and then analyzed by HP (C6890A) gas chromatography equipped with a DV-101 column (0.2 mm × 0.25 μm × 50 m) and FID detector. The injected volume was 0.2 μL. The external method was used to analyze and calculate the corresponding conversion and selectivity**.**

Results and discussion

Characterization of catalysts

A series of Cu-hydrotalcite (Cu-Fe, Cu-Al, Cu-Cr) catalysts were synthesized and the as-prepared Cu-hydrotalcite catalysts were initially characterized by XRD (**Fig. 1**). Sharp and intense diffraction intensity was observed for three synthetic samples, exhibiting the typical and symmetric HT reflections for the basal (003), (006), (009) and (110) **[23, 24]**. The (00*l*) reflections were characterized by high intensities combined with broad line shapes indicating that the resultant Cu-hydrotalcite were of relatively high crystallinity **[25]**.

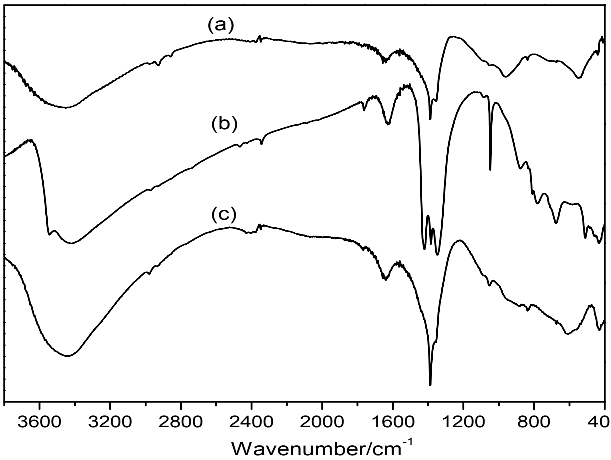


Fig. 2. FT-IR analysis of the resultant Cu-Al HT (a), Cu-Fe HT (b), Cu-Cr HT (c).

FT-IR analysis is a very useful tool to identify the presence of foreign anions in the interlayer of HT **[26, 27]**. FT-IR spectra of the synthesized HT catalysts were shown in **Fig. 2**. The two absorption bands observed at 1390 and 850 cm^{-1} indicated that the nitrate anion existed in the interlayer of the resulting HT **[25, 28]**. The nitrate anion would electrostatically interact with the positively charged layers, or with the water molecules, as suggested by the shoulder slightly above 3200 cm^{-1}. The absorption band centered at 3420 cm^{-1} was attributed to the band O-H stretching vibrations and the weak band near 1630 cm^{-1} was assigned to H-O-H bending vibrations mode were also presented due to the adsorption of water. Besides, the very weak band close to 2370 cm^{-1}, which was due to the influence of the unavoidable CO_2 during the synthetic procedure. The band at ~660 and 460 cm^{-1} were due to lattice vibrations involving the lamellar cations (Cu^{3+}, Fe^{3+} or Cr^{3+} or Al^{3+}).

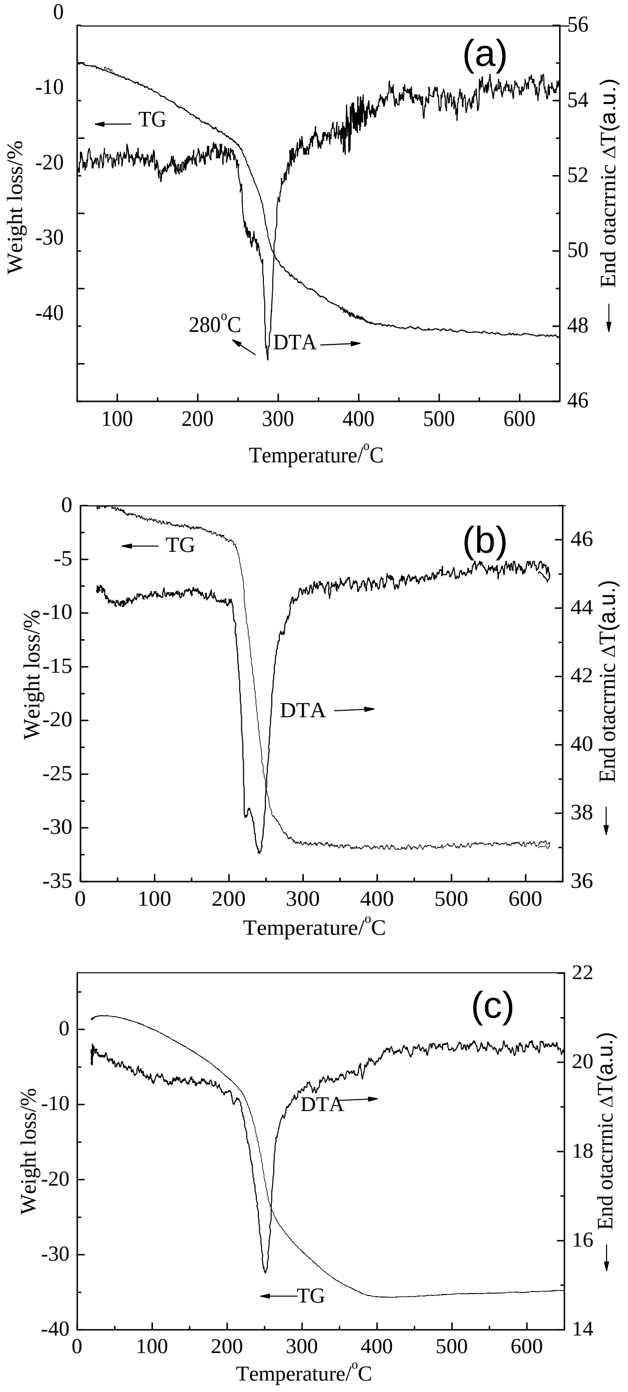


Fig. 3. TG-DTA analysis of the resultant Cu-Al HT (a), Cu-Fe HT (b), Cu-Cr HT (c).

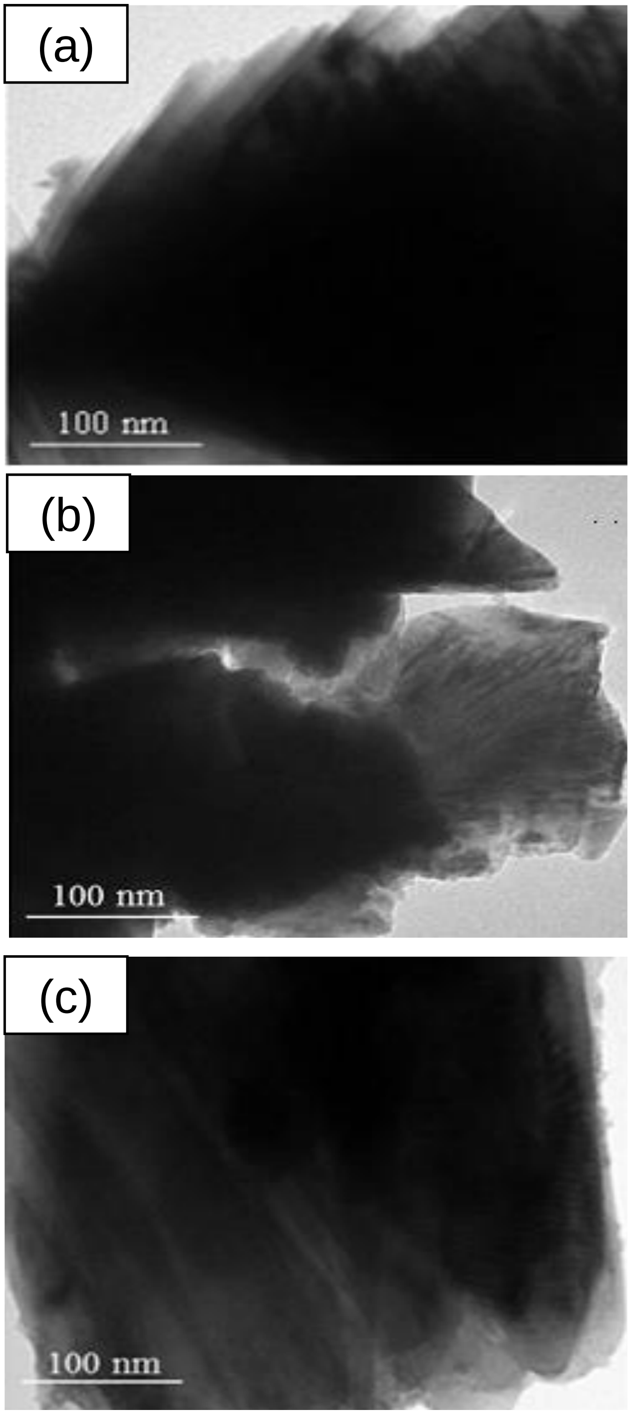


Fig. 4. TEM images of the synthesized Cu-Al HT (a), Cu-Fe HT (b), Cu-Cr HT (c).

The thermal stability of the resultant HT catalysts often presented influence on their catalytic application, TG-DTA analysis is thus used and the analysis profiles are given in **Fig. 3**. From the TG-DTA curve of Cu-Al HT catalyst (**Fig. 3a**), the material underwent a weak weight loss with an associated endothermic transition centered at 150 °C, corresponding to the loss of coordination or physisorbed water molecules, weakly bound to the materials. A clear weight loss (ca. 30 wt%) was located between 250 and 300 °C, observed as the second endothermal effect, which corresponded to the elimination of the hydroxyl groups and the removal of nitrate groups in the form of H_2O and NO_x **[29]**, thus transforming the layered Cu-Al hydrotalcite structure into a mixture of oxide phases with the layered structures collapsing **[29]**. In the TG-DTA curve of Cu-Fe HT catalyst, it display that two clear weight loss peaks located between 220 and 260 °C, which corresponded to the elimination of the hydroxyl groups and the removal of nitrate groups in the form of H_2O and NO_x, thus the structure of Cu-Fe HT was collapsed. For the case of Cu-Cr HT catalyst, the TG-DTA curve indicated that the hydrotalcite structure was destroyed at ~250 °C and a clear weight loss of ~35 wt% was ocurred. To understand the textural structure of the synthesized HT catalysts, TEM was further used as shown in **Fig. 4**. It was evident that all the synthetic Cu-HT catalysts presented a layered structure. A sheet stacking structure was very apparent in the case of Cu-Fe HT and Cu-Cr HT, which was a little weaker in the case of Cu-Al HT.

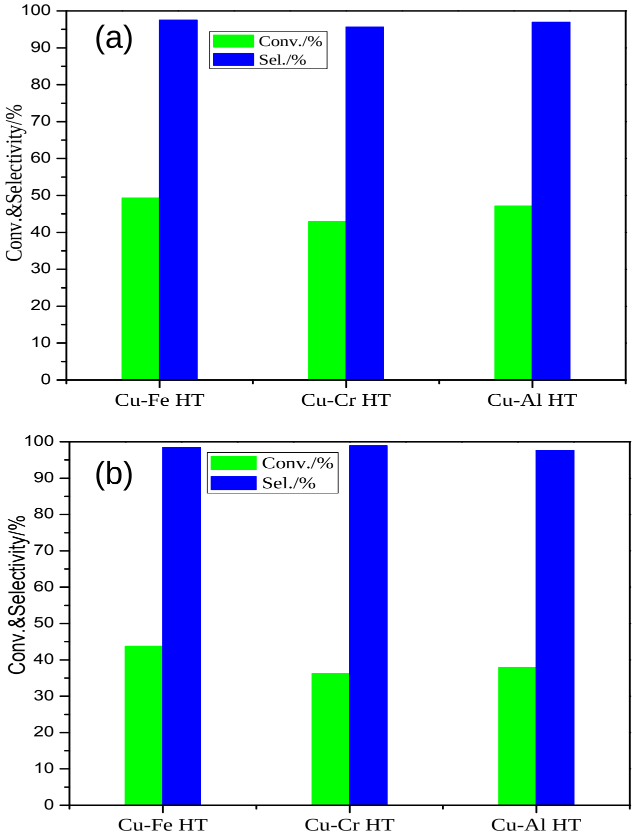


Fig. 5. Catalytic performances in synthesis of furfural diethyl acetal (A) and benzoin ethyl ether (B). ^{a} Reaction conditions: Sel.: the selectivity of furfural diethyl acetal; Conv.: the conversion of furfural. ^{b} Reaction conditions: Sel.: the selectivity of benzoin ethyl ether; Conv.: the conversion of benzaldehyde.

Catalytic performance in the synthesis of furfural diethyl acetal and benzoin ethyl ether

The resultant Cu-HT catalysts were initially employed for the synthesis of furfural diethyl acetal using heterocyclic aldehyde (furfural) with bioethanol. The catalytic results were shown in **Fig. 5a**. In general, three resultant Cu-HT catalysts display very high selectivity of furfural diethyl acetal, whereas over 96% selectivity was achieved. It was interesting to find very high selectivity of furfural diethyl acetal (~96%) was obtained in each case (**Fig. 5a**). The Cu-Al HT catalyst displayed the best activity, whereas 97.5% selectivity of furfural diethyl acetal was achieved at 49.3% conversion of furfural. To our limited knowledge, this is the best results have been achieved for the synthesis of furfural diethyl acetal on the heterogeneous catalyst. On the other side, the Cu-Cr HT catalyst presented the worst performance, whereby 96.9% selectivity of furfural diethyl acetal was obtained at 42.9% conversion. Besides, it was obviously to find that the influence from the incorporation of M^{3+} into Cu-hydrotalcite on the catalytic activity followed the order of Al^{3+} >Fe^{3+} >Cr^{3+}, which was possible due to the electronic interaction between Cu^{2+}, M^{3+} and the reactants **[30]**. In the blank reaction, nearly no formation of furfural diethyl acetal occurred with only ~8% conversion of furfural detected by our GC (not shown in **Fig. 5a**), which further confirmed the crucial role of Cu-HT catalysts.

To extend the application, the synthesized Cu-HT catalysts were further employed for the synthesis of benzoin ethyl ether using aromatic aldehyde (benzaldehyde) with bioethanol, the catalytic results were depicted in **Fig. 5b**. It was interesting to find that all the resultant Cu-HT catalysts continue to display good activities for the one-step synthesis of benzoin ethyl ether and very high selectivity (close to 98% in each case) was achieved. The best activity was achieved on Cu-Fe HT catalyst, whereby 98.4% selectivity of benzoin ethyl ether was achieved at 43.7% conversion of benzaldehyde. Meanwhile, the Cu-Cr HT catalyst exhibited the worst performance. In comparison with the previous results from literatures **[19, 20]**, our results are among the top-list.

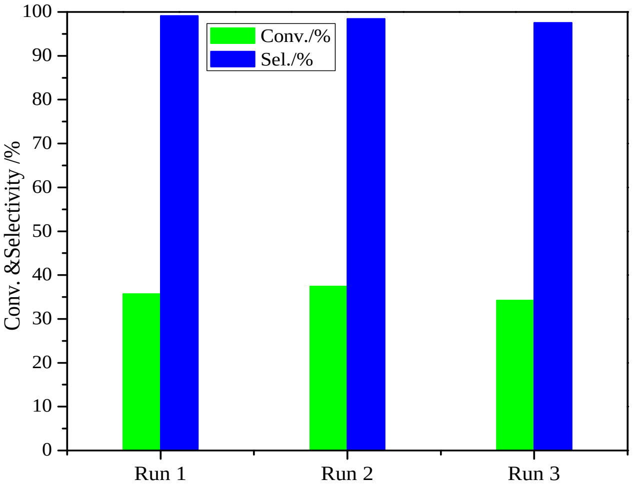


Fig. 6. Catalytic activity of the spent catalyst in the synthesis of benzoin ethyl ether.

Stability tests in the synthesis of benzoin ethyl ether

To further study the stability of the synthesized HT catalysts, the Cu-Cr HT catalyst exhibiting the worst performance in the second reaction of benzlaldehyde with ethanol was further chosen. The spent Cu-Cr HT catalyst was simply recycled through the centrifugation, washing with the solvent ethanol (6 mL) under the stirring condition and then drying at 110 °C overnight. After this procedure, the Cu-Cr HT catalyst was employed for the reaction. In our study, recycling the catalysts over three runs didn’t lead to any significant decline in terms of conversion and selectivity. Highly stable selectivity (over 97%) was obtained over three consecutive runs. For the first two runs (**Fig. 6**), the catalytic behaviour of conversion was very stable, whereby 35.7% conversion was in the first run and 37.1% conversion was in the second run. It was only in the third run that the conversion was marginally reduced to 33.0%. The ICP analysis of the aqueous reaction after the reaction showed no detectable leaching of metal cations even after the third run, which further confirmed nearly no leach of metal under the reaction conditions. Overall, all these results confirmed that the catalyst was stable and reusable.

Conclusion

In summary, a series of eco-friendly Cu-hydrotalcite (Cu-Fe, Cu-Al, Cu-Cr) catalysts were successfully fabricated. The catalytic results of the present study demonstrated that Cu-hydrotalcite catalysts were highly selective for the synthesis of furfural diethyl acetal and benzoin ethyl ether. The fabricated Cu-hydrotalcite catalysts maintained stable activities over several runs, which may be a good candidate for the reactions of aldehyde and bioethanol.

Acknowledgements

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