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Solvent-free oxidation of benzyl alcohol to benzoic acid by TBHP (ter-butyl hydro peroxide) using Co-Al hydrotalcite.

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ABSTRACT

Co-Al hydrotalcite containing Cl⁻ anion has been synthesized by co precipitation method and characterized by powder X-ray diffraction, scanning electron microscopy, FT-IR and thermo gravimetric analyses confirm a hydrotalcite-like structure and catalyse the oxidation of benzyl alcohol to benzoic acid in solvent free condition using TBHP as an oxidizing agent and hydrotalcite can be used recycle 3 times without lost its activity.

Keywords: Hydrotalcite, Heterogenous catalyst, Alcohol oxidation, Benzoic acid.

ARTICLE INFO

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1. Introduction

Conversion of benzyl alcohol to benzoic acid is chosen because it served as an intermediate in the biosynthesis of many secondary metabolites. Salts of benzoic acid are used as food preservatives and benzoic acid is an important precursor for the industrial synthesis of many other organic substances. Beside this benzoic acid is a suitable precursor for a number of fine chemicals, including phenol, caprolactam and benzoates salts and the currently industrial International Journal of Chemistry and Pharmaceutical Sciences

method to prepare benzoic acid involves high pressure and temperatures to perform the expensive and scarcely sustainable oxidation of toluene. [1] For this reason, in the last years a number of catalysts have been proposed to enable the oxidation of benzyl alcohol using hydrogen peroxide as an eco-friendly oxidant to access benzoic acid. Lee et al used Pd-Au bimetallic system [2], Koonning et al used Cu [3], Saisaha et al used Mn containing catalysts system [4],

Karthikeyan et al used CuCl_2/Bil catalytic system [5]. Layered double hydroxides are the anionic clay in which divalent cations within brucite-like layers are replaced by trivalent cations. The resulting positive charge is compensated by hydrated anions located in the interlayer space between two brucite sheets. The general formula for these materials is $[\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2]^{x+}[\text{A}^{n-}]_x \cdot n\text{H}_2\text{O}$, where M(II) and M(III) are di- and trivalent metal cations, respectively, which occupy octahedral positions in hydroxide layers; A^{n-} is an exchangeable anion, such as CO_3^{2-} , NO_3^- and Cl^- , etc. [6–9]. Due to heterogeneous catalyst it offers several advantages over homogeneous ones, such as an ease of recovery and recycling atom utility and enhanced stability in the oxidation reaction.

A few studies on liquid phase oxidation of benzyl alcohol and benzaldehyde using heteropolyacids [10], Ni-Al and Ru-Co-Al hydrotalcite [11,12,14] showed good catalytic activity in the benzyl alcohol oxidation by molecular oxygen in the presence of solvent. But in our knowledge there is no report on the oxidation of benzyl alcohol to benzoic acid using hydrotalcite as a catalyst. There is little known about the oxidation of alcohol with TBHP over heterogeneous catalysts. Catalytic oxidation with TBHP as an oxidizing agent is particularly attractive from an economical and environmental point of view [13]. Since the LDHs containing transition elements showed very high H_2O_2 decomposition activity at the oxidation conditions. TBHP was chosen as the oxidizing agent in the present studies. Besides benzoic acid, the oxidation of benzyl alcohol can theoretically afford three different compounds, the aldehyde as an intermediate oxidation product and the ester as a product of the oxidation of the hemiacetal intermediate arising from the condensation between benzyl alcohol and aldehyde. Therefore, this inspired us to investigate their catalytic activity for selective oxidation of benzyl alcohol to benzoic acid.

The present work was undertaken with the objective of investigating the liquid phase oxidation of benzyl alcohol to benzoic acid in the absence of any solvent using a number of synthetic hydrotalcite like materials. LDHs containing one or two different transition elements (viz Ni, Co, Zn, Cu, Fe, Mn) and TBHP as an oxidizing agent is used for the oxidation of benzyl alcohol. In order to identify and develop the best catalyst for the oxidation of benzyl alcohol to benzoic acid a series of hydrotalcite containing different transition metal were examined. The best result was found with Co-Al hydrotalcite and then a series of different ratio of Co-Al hydrotalcite have been studied and hydrotalcite best with 3:1 ratio.

2. Materials and Methods

Catalyst Preparation: The layered double hydroxide and/or mixed hydrotalcite containing different divalent metal M(II) and trivalent M(III) metallic element with M(II) /M(III) mole ratio of 2.0,3.0 and 4.0 having different anions (Cl^- , NO_3^-) were prepared as follows: two aqueous solutions one containing metal salt solution of divalent metal and 2nd metal salt solution of of trivalent metal were added dropwise NaOH solution with maintaining pH 10-11 in a round

bottom flask within one hours stirring with heating and two hours only heating on reflux and obtained slurry filtered and washed with distilled water and dried in oven at 100°C for 24 hours. Obtained hydrotalcite were used for oxidation of benzyl alcohol using TBHP as an oxidizing agent.

Characterization of the Catalyst

The structures of the catalysts were studied by XRD, FT-IR, SEM and TGA methods. PXRD was carried out in a Philips X^oPert MPD system using Cu K radiation ($\lambda = 1.5406 \text{ \AA}$). The operating voltage and current were 40 kV and 30 mA, respectively. FT-IR absorption spectra of the samples were recorded in a Perkin-Elmer FT-IR spectrometer (Model-FT-1730). The powdered samples were ground with KBr in 1:20 ratio and pressed into pellets for recording the spectra. Thermo gravimetric analysis (TGA) was carried out in Mettler TGA/SDTA 851e and the data were processed using Stare software, in flowing nitrogen in a flow rate of 60 ml/min and at a heating rate of $20^\circ\text{C}/\text{min}$. The electron microscopic study has been done with scanning electron microscope (Leo series VP1430). The samples were coated with gold using sputter coating before analysis to avoid charging effects during recording. Analyses were carried out with an accelerating voltage of 20 kV and a working distance of 17 mm, with magnification values up to 100,000 xs.

Catalytic Reaction

The catalytic oxidation of benzyl alcohol over the hydrotalcite catalysts was carried out in a magnetically stirred round bottom flask (100), provided with a mercury thermometer for measuring the reaction temperature and reflux condenser, at the following reaction conditions. Reaction mixture: 10.4 mmol benzyl alcohol; 27.2 mmol TBHP; 0.1g catalyst; bath temperature, $90+_{-}100^\circ\text{C}$; reaction time, 3h. After the reaction the catalyst was removed from the reaction mixture by filtration and measuring the catalysts performance for the oxidation as function of time, liquid samples were removed time-to-time from the reaction mixture by syringe and monitored by TLC.

In order to identify and develop the best catalyst for the oxidation of benzyl alcohol by using TBHP as an oxidizing agent a study on various hydrotalcite catalysts have been studied. A series of hydrotalcite containing different transition metal were examined. The best result was found with Co-Al hydrotalcite and then a series of different ratio of Co-Al hydrotalcite have been studied and hydrotalcite best with 3:1 ratio. (Table.1). Al-Co-Cl hydrotalcite is also applied for the conversion of aldehyde to corresponding acid. In this benzaldehyde, convert benzoic acid with good yield (100%). Table 2 shows the oxidation of aldehyde to their corresponding acid.

Table 1: Oxidation of Benzyl alcohol using various Hydrotalcites^a

run	catalyst	(%) Yield of benzoic acid
1.	Al-Co- NO_3^-	80
2.	Al-Cu- Cl^-	39
3.	Al-Mn- Cl^-	56
4.	Al-Co- Cl^-	94
5.	Al-Mg- Cl^-	-

6.	Ru-Co-Al-Cl	83
7.	Calcined Al-Co-Cl	-

^aReaction Condition: benzyl alcohol, 10.4 mmol; TBHP, 27.2 mmol; catalyst, 0.1 g; temperature, 90+100°C; time, 3h;

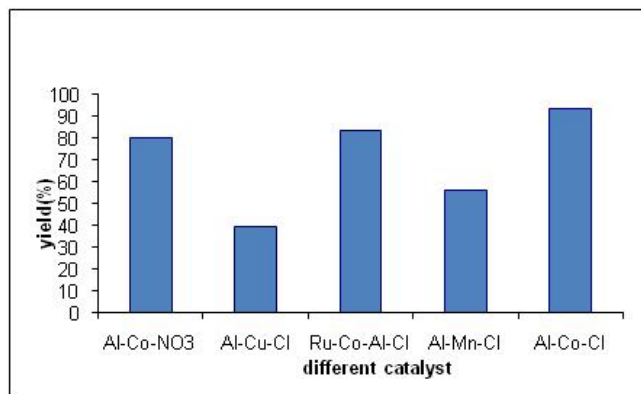
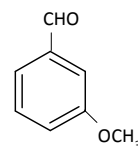


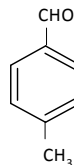
Figure 1: Oxidation using various hydrotalcite

Table 2: Oxidation of aldehyde to corresponding acid^a

run	aldehyde	Yield of corresponding acid (%)
1.		100
2.		80
3.		-
4.		100
5.		100



6.



55

^aReaction Condition: aldehyde, 10.4 mmol; TBHP, 27.2 mmol; catalyst, ^aReaction Condition: aldehyde, 10.4 mmol; TBHP, 27.2 mmol; catalyst

3. Results and Discussions

Table-1 show in all hydrotalcite Al-Co-Cl hydrotalcite gives best result. All Hts catalysts have been characterized for their crystalline structure and morphology and anion and thermal behavior. Detailed study has been done of Al-Co-Cl- hts since it show good catalytic activity in oxidation of benzyl alcohol to benzoic acid.

Crystal structure of Al-Co-Cl hydrotalcite

Fig. 2 shows XRD patterns of the Co-Al-LDH with the Co/Al molar ratio 3. As seen from Fig. the diffraction peaks (at 2θ 14.5°, 31.8°, 38.6° and 40.1°) of Co-Al-Cl are accordingly corresponding to the relations of (003), (006), (009) and (110). [15, 16] The diffraction peaks which are narrow, sharp and symmetrical suggest that the sample is well-crystallized. Meanwhile, the strongest diffraction peak which appears at 2θ 14.5° indicates the Co-Al-LDH crystals grow along the (003) and develop a typical hexagonal crystal structure like hydrotalcite compound.

FTIR studies: Fig. 3 shows FT-IR spectra of the Co-Al-LDH with the different Co-Al molar ratio 3. As seen in the broad peak around 3520 cm⁻¹ can be attributed to the stretching of OH⁻ attached to metal ions. The peak of the bending vibration of interlayer water appears at 1615 cm⁻¹. A small band is observed at 1718 cm⁻¹ just next to the water bending vibration at 1615 cm⁻¹. The peaks appearing between 400 cm⁻¹ and 750 cm⁻¹ are ascribed to the vibration of Co-Al-LDH lattice (Al-O, Co-O).[17]

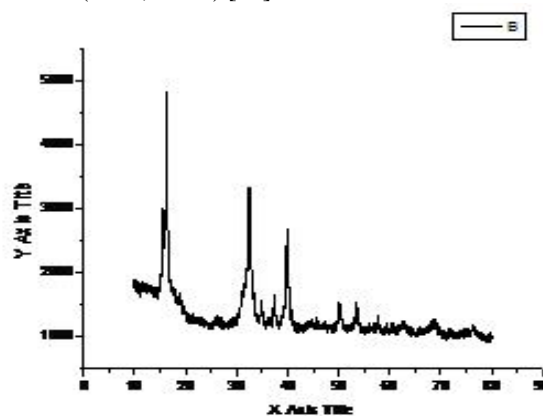


Figure 2: P-XRD of Al-Co-Cl- hts

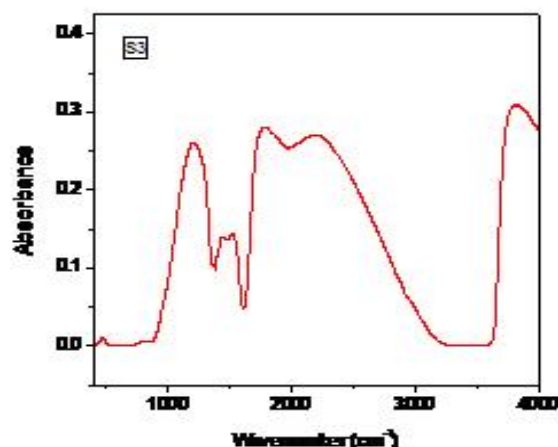


Figure 3: FT-IR spectra of Al-Co-Cl hts

Thermal behavior

Fig 3 show the thermal decomposition of the sample occurs in two well-defined endothermic steps. The first step, near 150°C, is ascribable to the endothermic loss of co-intercalated water. [18] The second step, near 250°C, is attributed to the loss of constitutional water and of CO₂ and leads to the formation of mixed metal oxides. Above 300°C a very limited weight loss is observed, due to the loss of surface species such as hydroxyl groups and surface chloride anions.

Morphology of Hydrotalcite

Fig.4 shows the typical SEM image for Co-Al 3:1 (molar ratio) Co-Al-LDH. As seen in Fig., the existing lamellar has a hexagonal shape which is the typical structure of the hydrotalcite like material [19].

Oxidation of benzyl alcohol

Table-1 show the result of oxidation of benzyl alcohol with various hydrotalcites it concluded from table Ru-Co-Al-Cl give 83% yield of product in 5 hrs and Al-Co-NO₃⁻ give 80% in 3 hrs but the best result is obtained with 94% yield in 3 hrs shown in figure 1. and table-2 shows a series of oxidation of aldehyde to their acid, m-chloro benzaldehyde oxidized into m-chloro benzoic acid with 80% yield but p-hydroxy benzaldehyde do not oxidized due to the opposition of hydroxyl group, O-nitro benzoic acid and 3-methoxy benzoic acid occur with 100% yield.

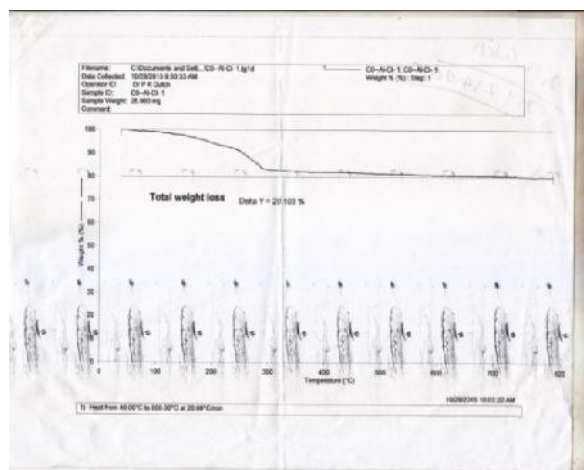


Figure 4: TG spectra of Al-Co-Cl hts

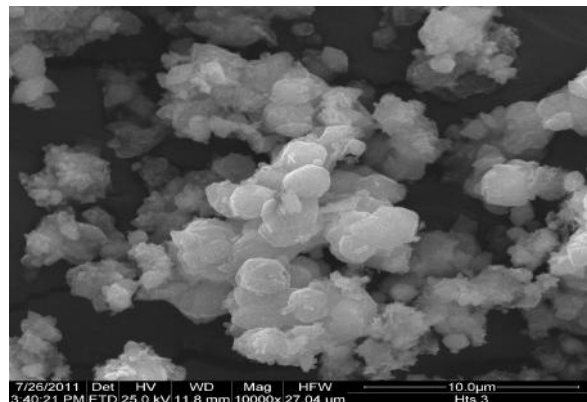


Figure 5: Sem image of hts

Characterization of benzoic acid

Benzoic Acid has been characterized according to the results of the ¹H and ¹³C-NMR spectral analysis performed in a Bruker DRX-400 and herein reported *Benzoic acid* (3). White solid, 99% yield, m.p. 122 °C ¹H-NMR (CDCl₃) : 7.49 (dd, 2H, *J* = 7.6 and 6.8 Hz), 7.63 (t, 1H, *J* = 6.8 Hz), 8.13 (d, 2H, *J* = 7.6 Hz), 11.88 (brs, 1H); ¹³C-NMR (100 MHz, CDCl₃) : 128.5, 129.3, 130.2, 133.8, 172.5.[20]

Recycling of the Catalyst:

Hydrotalcite can be recovered easily from the reaction media by simple filtration after the reaction and could be reused for the next run (table-3). In the first two run it is used as a good catalyst it repeat two times with same yield i.e. 94% and in 3rd run the yield has been decrease.

Table 3: Recyclability of catalyst

run	Time(hours)	Yield of acid (%)
1.	3	93
2.	3	93
3.	3	57

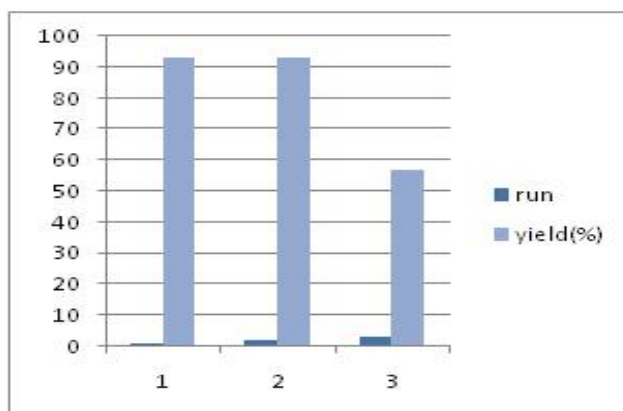


Figure 6: Recyclability of catalyst

4. Conclusion

In conclusion the hydrotalcites having Co cation and Cl anion (Al-Co-Cl) was found to be an effective heterogeneous catalyst for the oxidation of benzyl alcohol and aldehyde to their corresponding acid. Use of TBHP as an oxidizing agent, the simple work-up procedure, the

reusability of the hydrotalcite catalyst and solvent free condition make this oxidation as an environmentally benign chemical process.

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