RESEARCH ARTICLE

AN EFFICIENT HETEROGENEOUSLY CATALYSTED SYNTHESIS OF 3-ACETYL COUMARIN IN WATER

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ARTICLE INFO	ABSTRACT
	This communication report knoevenagel cyclo-condensationusing hydrotalcites prepared using various methods. Further, the hydrotalcite providing maximum yields was used for the synthesis of 3 acetyl coumarin. In this multi-component reaction the yields obtained with Mg-Al-CO$_3$ LDH was 94% and with the unreported Ca-Al-CO$_3$ LDH was 93% respectively. The reaction conditions being 2 wt% catalysts at 80^{0}C for only 90 minutes. The main benefit of the present work is reduction of time along with the catalyst used is environmentally benign, recyclable and easy to work up procedure using water as green solvent. The catalysts as well the products were subjected to various characterization being X-RD, TGA, FT-IR, SEM, NMR, Mass, and basicity respectively.

INTRODUCTION

In the process of developing and synthesizing various fine chemicals and pharmaceuticals, there are several steps involved acquiring larger reagent quantities using functionalizing agents, mineral acids and bases. Thus, results exhibit larger E-factor. The valuable raw materials were wasted thus making the waste treatments essential as well as expensive. Due to the increase in the yields of by-products the overall economic value of the product is decreased. Primarily the main aim was to develop an alternative route for its synthesis which was environmentally benign. In attaining an environmental friendly process the role of heterogeneous catalysts displays importance as they have various benefits being their operation is safe, reduces wastes, along with this their work up is also very easy. Therefore the development of mixed oxides and other clay type material i.e. hydrotalcites have been established (Sheldon, 1997; Thomas, 1992; Dartt, 1994; Hattori, 1995; Ono, 1997 and Cavani, 1991). Hydrotalcites are clay materials which are represented by the chemical formula $Mg_6A_{l2}(OH)_{16} \cdot 4H_2O$. they find application as anionic clays and are applied as catalysts, support of catalysts, ion-exchange and composite materials. When their calcinations takes place at 723 K, highly basic mixed metallic oxides are formed with the surface area being moderate working as efficient catalyst for the several base catalyzed condensation reactions (Lakshmi Kantam, 1998; Corma, 1990 and Martín-Aranda, 1995).

Since many decades coumarins and all the compounds related to coumarins have exhibited various significant and important medicinal and therapeutic potentials. There are several methods using which these coumarins can be synthesized being Perkin, Wittig, Pechmann, Reformatsky, Clasein, Knoevenagel and flash vaccum pyrolysis reaction (Roderiguez, 1998; Pechmann, 1884; Johnson, 1942; Brufola, 1996; Shirner, 1942; Yavari, 1998 and Cairns, 1994). Thses coumarins exhibit several versatile biological activities being antioxidation, anti-HIV, Antitumor, anti-cancer as well as antimicrobial activity (Weber, 1998; Patil, 1993; Yun, 2001; Zaha, 2002 and Maly, 2002). There are several derivatives of coumarins which function as anti-tumor, anti-platelets being warafins, psoralen etc. The synthesis of coumarins involve extreme condition and multiple steps. The work up procedure is also lengthy. There is a great significance of using base catalysts in this synthesis. In the current work we, synthesized 3 acetyl coumarin in shorter duration which has not been reported yet. The synthesis of the same product with Mg-Al-CO$_3$ has been reported by Chanda et.al and the time taken for their synthesis was calculated to be minimum 3-4 hours and the time taken by the catalys synthesized in the present study was observed to be 90 minutes. The use of Ca-Al-CO$_3$ in the synthesis of 3 acetyl coumarin has not yet been reported. The yield obtained by both the catalysts was more than 93%. The reported yields of other researchers were observed to be 83% and 85% respectively. Further, the amount of catalyst used by them was also in larger quantity then ours, they used 10 wt % catalysts and the present study uses 2 wt% catalysts. The solvent used by Chanda *et al.* was toluene (30 ml) whereas in the present research work water has been used as a green

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solvent and the amount used was reduced from 30 ml to 10 ml. The hydrotalcite reported by Chanda *et al.* was synthesized using co-precipitation method taking longer duration of time and energies whereas our best results were obtained using the grinding method, exhibiting the minimum and extreme reduced duration without using any electrical energies in the synthesis. The yields obtained in their research work of the products were calculated to be 83% and the yield obtained in our research was 94%. Finally, last but not the least, the recyclability of the catalyst in their research work was almost negligible and in our research work the recyclability of the catalyst was found to be 6 times maintaining the yield of the end product. This recyclability mainly enhanced the efficiency of the catalyst along with this the cost of the product was also reduced. The use of hydrotalcite exhibit the use of hydrotalcites as green catalysts in the synthesis of coumarins biologically active materials (Hoefnagel, 1995). In this current work coumarins were efficiently synthesized in lasser duration and at lower temperatures with higher yields.

MATERIALS AND METHODS

Synthesis of the Catalyst: Various methods have been used for synthesizing hydrotalcites in various ratios. The methods are as follows:

a)Grinding Method: In this method, first the oxides were taken and suspended in 2 ml distilled water further adding the accurate amount of measured hydroxides maintaining the pH at 8. Some sodium bicarbonate was added to further enhance the pH to 10. For next 5 minutes the mixture was taken and grinded in mortar and pestle. Further, it was washed with distilled water several times to remove all the impurities and dried at 100^0C and calcined at 723 k for another 1.5 hours.

b)Hydrothermal Method : The hydrotalcite synthesized using this method were made at high temperatures and pressures in aqueous media using a pressure reactor. The measured amounts of alumina and magnesium hydroxides were taken and mixed in 100 ml distilled water maintaining the pH by 8.5. The pH was maintained by dropwise addition of sodium bicarbonate solution. This solution was further transferred to a pressure reactor of 300 ml and was aged for 6 hours maintaining the temperature at 175^0C. On obtaining the precipitate, it was washed and filtered again and again for removing the impurities and further dried overnight and then was calcined at 723 k for 4 hours.

c)Co-Precipitation Method: In this procedure the M^{2+} and M^{3+} nitrate cation solutions were taken and added separately in distilled water. The pH was maintained at 11-12 by dropwise addition of sodium hydroxide solution. The reactants were heated at 80^0C for 3 hours in which in the first hour both stirring and heating both were done and further in the next two hours only heating was done switching off the stirring part. After 3 hours the solution was filtered, washed, precipitated, dried and calcined at 723 K for 1.5 hours.These hydrotalcites prepared were further characterized using XRD, FT-IR, TGA, SEM and basicity. Comparison of yield synthesized different method of hydrotalcites as given (Table 1-2)

EXPERIMENTAL PART

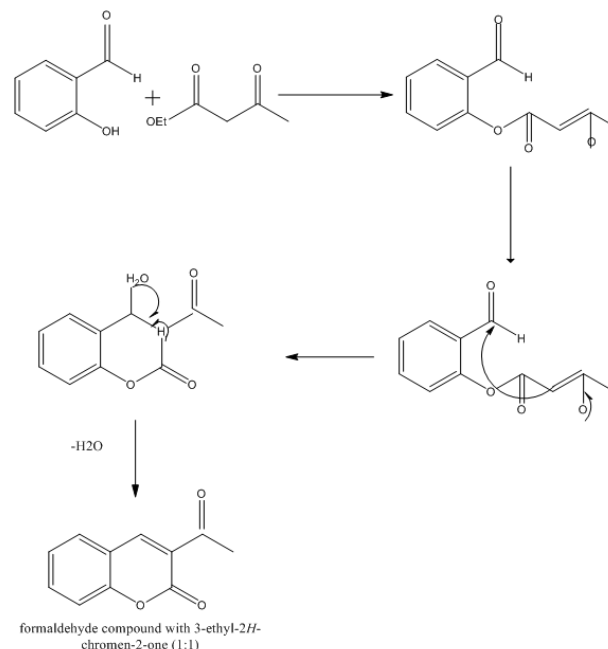Melting points were taken on Gallen kamp melting point apparatus and were uncorrected. Thin layer chromatography was performed with fluorescent silica gel plates HF254 (Merck), and plates were viewed under UV254 and 265 light. Infrared spectra (λ-cm-1) were recorded on Perkin Elmer FT-IR Spectrophotometer, using KBr disks, Mass spectra are measured on LCMS-8030 and 1H-NMR spectra were recorded on Gemini-200 MHZ NMR spectrometer in DMSO-d6 and spectra were internally referenced to TMS. Peaks are reported in ppm.

Synthesis of the Coumarin: In a round bottom flask 2 mmol of salicyladeyhde and 2 mmol of ethylacetoacetate were added together and mixed homogeneously. To the mixture 10 ml water was added as a solvent. To the aforementioned mixture freshly prepared hydrotalcite catalysts was added by 2 wt% ratio and the temperature was maintained at 80^0C for 90 minutes. The precipitate obtained was thus filtered off, washed and re-crystallized with ethanol. The purity of compounds was investigated and established using TLC plates. The yields obtained for the aforementioned products were calculated to be more than 93 % with both the catalysts. This will be discussed in detail in results and discussion section. The product was further characterized using FTIR, Mass and NMR.

Scheme1

SALICYALDEHY   ETHYLACETOACETATE   3-ACETYLCOUMARIN

Mechanism of scheme 1

-H2O
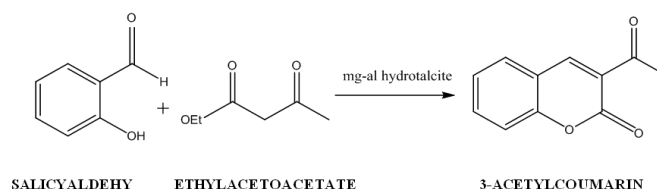
formaldehyde compound with 3-ethyl-2*H*-chromen-2-one (1:1)

RESULT AND DISCUSSION

Basicity of the hydrotalcites: J. Lal *et al.* The basicity of the hydrotalcites was found in the range of H_ 9.3-15 (Lal, 2012). On the surface of the hydrotalcites two types of basic sites were found between H_ 7.2 -9.8 and H_ 9.3-15 exhibiting two types of surface active basic sites existing in hydrotalcites. The strong basic sites as attained by pure oxides are due to the predominance of O_2- but the calcines ones exhibit surface basic sites.

**Table 1. Yields and various metal ratios of Mg-Al-X Hydrotalcite**

S. No.	Ratio Al: Mg	Chemical (I) Al$_2$O$_3$	Chemical (II) Mg(OH)$_2$	Grinding Method (Yield)	Hydrothermal Method (Yield)	Co precipitation Method (Yield)
1.	1:2	1.02 g	1.16 g	3.455 g	1.455 g	3.892 g
2.	1:3	1.02 g	1.74 g	5.635 g	2.805 g	5.984 g
3.	1:4	1.02 g	2.32 g	6.020 g	3.020 g	7.202 g

Table 2. Yields and various metal ratios of Ca-Al-X Hydrotalcite

S.N.	Ratio Al:Mg	Chemical (I) Al$_2$O$_3$	Chemical (II) Ca(OH)$_2$	Grinding Method (Yield)	Hydrothermal Method (Yield)	Co precipitation Method (Yield)
1.	1:2	1.02 g	3.8 g	4.087 g	2.155 g	4.572 g
2.	1:3	1.02 g	4.5 g	6.415g	4.605 g	7.283 g
3.	1:4	1.02 g	5.2 g	6.154 g	3.422 g	7.189 g

Table 3. Optimization of reaction condition for synthesis of 3-Acetylcoumarin under water solvent condition at 80^{0}C temp. using Mg-Al hydrotalcite catalyst

Name of Catalyst	Catalyst in mg	Yield(%) of product
Mg-Al-CO$_3$	0.05 mg	40
Mg-Al-CO$_3$	0.1 mg	65
Mg-Al-CO$_3$	0.2 mg	94
Mg-Al-CO$_3$	0.4 mg	78
Mg-Al-CO$_3$	0.5 mg	72
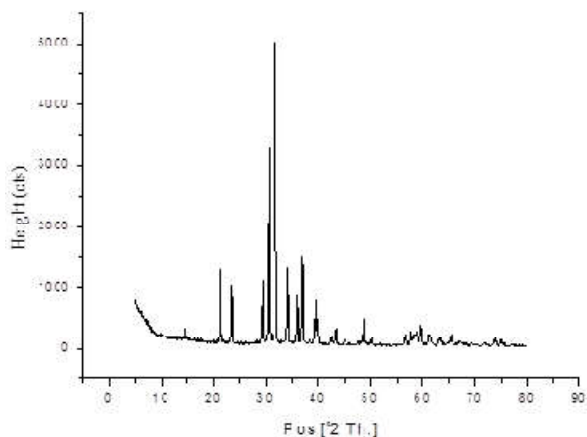
Fig. 1.
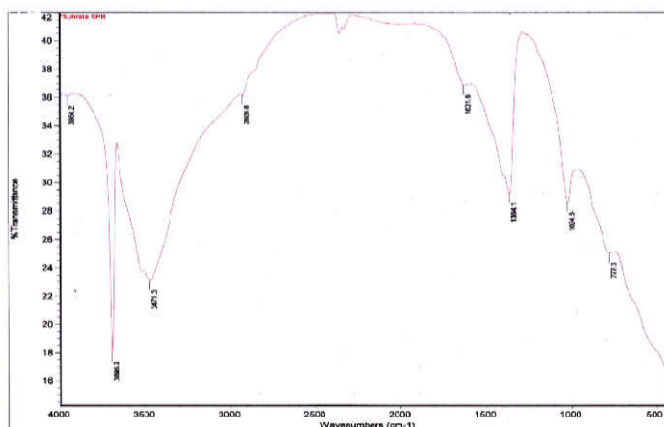
Fig. 2.

Our view was supported by Di Cosimo *et al*. The detailed investigations of the basicities were performed on two hydrotalcites being Mg-Al and Ca-Al. in the Mg-Al hydrotalcites, on further increasing the molar ratio of Mg-Al to 3:1 the total basicity also increased. On further enhancing the molar ratio from 3:1 the loss of catalytic activity was noted further decreasing the basicity. Many other researchers supported our view viz Nakatsuka T et.al and Fishel et.al. They measured basicity using different methods being benzoic acid method, CO$_2$ TPD method etc. Basicity measured by many researchers via various methods depicted the same results that maximum basic site density was observed in the Mg-Al ratio of 3:1.

Basicity of LDH

1.	Mg-Al CO$_3$ (3:1)	9.3 < H_ < 15
2.	Ca-Al-CO$_3$ (3:1)	9.3 < H_ < 15

Characterization of Mg-Al-CO$_3$

XRD: As exhibited in the figure (1) below the d value obtained are 7.76 Å which is in excellent agreement with the reported values of LDH carbonate.

The calculated height of the gallery was found to be 2.36 Å along with the height of the cationic sheet 4.8 Å. The synthesized LDH displays well ordered agreement as well as good crystillinity. The size of the crystallite was found to be 24.87 nm. According to the quoted literature [48] the size of the crystallite prepared by the hydrothermal method was comparatively low, c=23.28 Å for the 003 peak position. Because of the high electrostatic interactions the interlayer spacing in between the Mg/Al layer and CO$_3$$^{2-}$ was found to be lower.

FT-IR: The Mg-Al-CO$_3$ hydrotalcite were characterized using FT-IR with a metal ratio of 3:1 is exhibited in the following fig -2. In the figure, a broad band is visible at 3700-3500 cm^{-1} ascribing to the hydroxyl group vibration band. Intermolecular hydrogen bonded OH group exhibits peak at 3471 cm^{-1}. At 3200 cm^{-1} a weak peak is observed ascribing to the OH stretching mode of interlayer water molecule. A band at 1631 cm^{-1} is ascribed to absorbed interlayer molecule. The antisymmetric stretching of inter carbonate layer band was observed at 1364 cm^{-1}. Exhibiting bond shift as amongst the hydroxyl sheets and water molecules present in between the interlayer exist strong bonds of hydrogen. A bending vibration band is observed at 1632 cm^{-1} which is due to the adsorbed

water interlayer of δ HOH. Some impurities of NO_3^- present from solution are depicted at 1383 cm^{-1}. The carbonate bands are observed below 1000 cm^{-1} at 777.3 cm^{-1} and 443.3 cm^{-1} respectively. The weak bands are ascribed to the CO_3^{2-} ions as they form stable anionic clays.

TGA: As it can be seen from the figure-3 the TGA curves of the Mg-Al hydrotalcite depicts total loss of 38.26% weight. The stability of the prepared hydrotalcites shows that they are thermally stable till 230 ^0C temperature. The total weight lost is between the temperatures 330 -670^0C. the weight loss takes place in three faces between 60-230^0C, 230-330^0C, and 570°C-670°C respectively. If further weight loss is exhibited below this temperature then the reason behind it is external water surface and inter-lamellar water molecules. This view is supported by literature. The weight which is lost between the temperatures 230-330^0C is ascribed to the de-hydroxylation of brucite layers along with the decomposition of anion leaving Mg, Al hydroxide behind. The weight loss exhibited between the temperatures 570°C-670°C is due to the continuous elimination of hydroxyl ions producing the metal oxides and spinal structures.

SEM: The SEM image of Mg-Al-CO$_3$ with a metal ratio of 3:1 is shown in the following Figure (4). The image exhibits materials which are round and hexagonal in shape of lamellar existence, a structure of typical hydrotalcite.
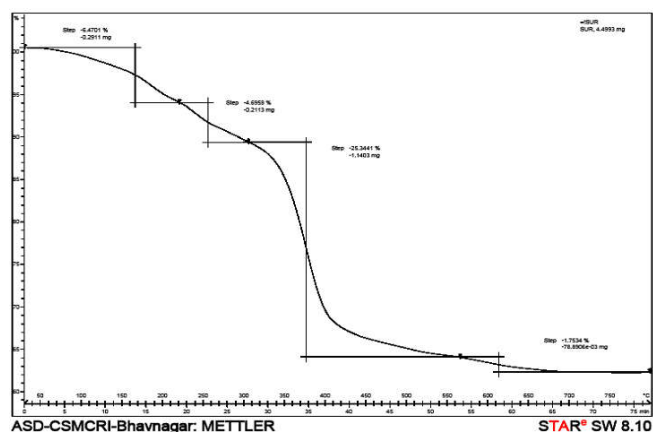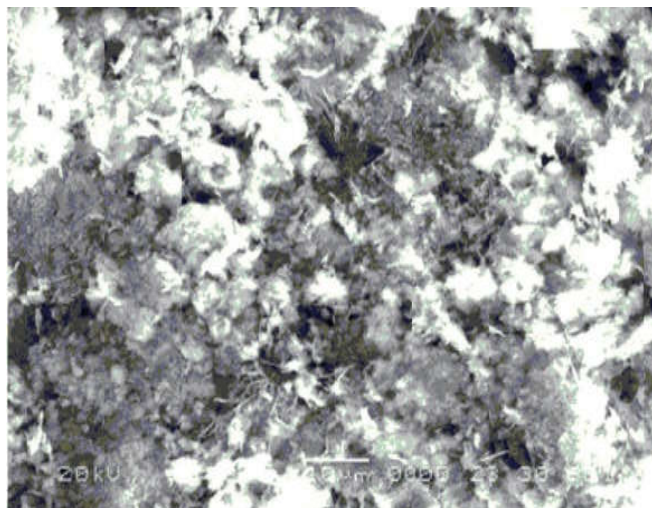

Fig. 3.

Fig. 4.

Characterization of Ca-Al-CO$_3$

XRD: The XRD patterns Fig. (5) for the Ca-Al-CO$_3$ hydrotalcites exhibits 29.03 Å lattice parameter c, which was calculated on the basis of the strongest crystallographic indices 003 position, the lattice distance d003. The d 001 reflection was calculated to be 3.03 Å. A rombohederal cell were indexed by their reflections. The Scherrer formula was used for calculating the crystallite size and was found to be 47.035 nm. High crystallinity was depicted by our prepared hydrotalcites but the crystallite formed was small as shown in Figure (5). Our findings have been supported by many researchers who have reported similar trends of the diffraction maxima in literature.
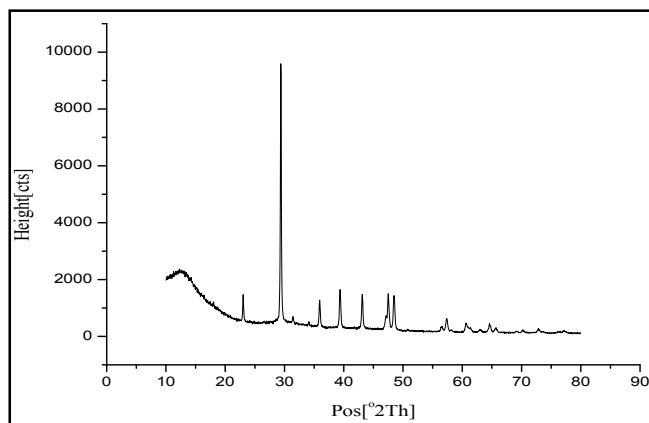

Fig. 5.

Table 4. Effect of solvents on the synthesis of 3-Acetylcoumarin in the presence of Mg-Al hydrotalcite Catalyst

Solvent	Time (min)	Yield (%) of product
Water	90 min	94
Methanol	120 min	77
Ethanol	120 min	78
Acetone	135 min	63
Acetonitrile	150 min	55

Table 5. Different temprature effect on the synthesis of 3-Acetylcoumarin in the presence of Mg-Al hydrotalcite Catalyst with water solvent

Temprature ^0C	Time (min)	Yield (%) of product
Room temperature	155 min	30
60^0C	105 min	67
80^0C	90 min	94
100^0C	90 min	86
120^0C	90 min	80

FT-IR: In the FT-IR of Ca-Al Hydrotalcite with a metal ratio of 3:1 a broad peak is observed at 3440 cm^{-1} in the figure-6, along with this two shoulder peaks can also be seen at 3567 and 3062 cm^{-1} which are ascribed to the υ OH stretching bands of water. The peaks which are recorded between 1639- 1531 cm^{-1} are ascribed to δH2O. a broad peak is attained because of strong H bonds existing amongst OH groups and water molecules. Interlayer carbonate anions are recorded at 1400 cm^{-1}. The free anion band is recorded at 1450 cm^{-1} showing the shift in band due to the H bonding amongst the OH groups and the water molecules. Some weak bands are also observed at 871 cm^{-1} and 679 cm^{-1} which are ascribed to υ2 and υ4 stretch of the CO_3^{2-}.

Table 6. Effect of different methods of synthesis Mg-Al hydrotalcite Catalyst on the synthesis of 3-Acetylcoumarin

S.N.	Methods	Catalyst amount	Time	Solvent	Yield (%)
1.	Co-precipitation	0.2 mg	90 min	Water	83
2.	Grinding	0.2 mg	90 min	Water	94
3.	Hydrothermal	0.2 mg	90 min	Water	78

Table 7. Effect of different methods of synthesis Ca-Al hydrotalcite Catalyst on the synthesis of 3-Acetylcoumarin

S.N.	Methods	Catalyst amount	Time	Solvent	Yield (%)
1.	Co-precipitation	0.2 mg	90 min	Water	81
2.	Grinding	0.2 mg	90 min	Water	93
3.	Hydrothermal	0.2 mg	90 min	Water	76

Comparison of others work Table 8 (compare other work)

S.N.	Catalyst	Time	Yield	Remark	Reference
1.	Piperidine	5 min	98%	Difficult to separate	(Siddiqui, 2009)
2.	Heteropolyacids	120 min	98%	Difficult to separate	(Majid, 2008)
3.	Zn[(L)-Proline]₂	15 min	92%	Difficult to separate	(Jayaseelan1, 2015)
4.	Piperidine	2-3 hr	89%	Difficult to separate	(Arjunan, 2013)
5.	Mg-Al hydrotalcite	4 hr	83%	More time and lasser yield	(Ramani, 1999)
6.	Diethylamine	15-20 min	78%	Strong base difficult to separate	(KUMAR, 2012)
7.	n-isopropylamine	40-45min	46%	Strong base difficult to separate	(Baghernejhad, 2016)
8.	Nano-TiO2	1.5 hr	98%	High cost	(Ranu, 2006)
9.	[bmIm]OH	15min	88%	Difficult to separate	(Heravi, 2008)
10.	Mg-Al hydrotalcite	90 min	94%	Easy to separate	Present work
11.	Ca-Al hydrotalcite	90 min	93%	Easy to separate	Present work
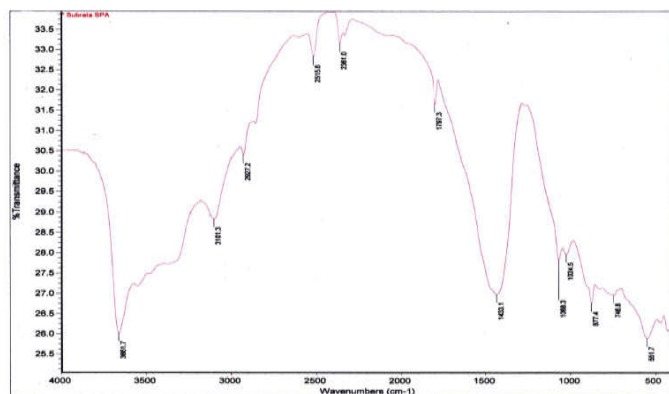
Fig. 6
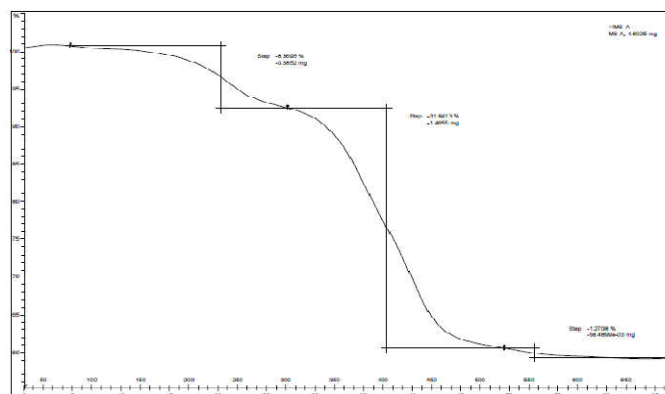
Fig. 7.

TGA: As shown in the figure below, the TGA graph (7) of Ca-Al-CO$_3$ hydrotalcite exhibits a total loss of 50.71 %. There are two steps in which the weight loss took place. The first weight loss exhibited a total of 10.46% starting from 55 - 300^{0}C because of elimination of molecular water from its interlayers. The second weight loss exhibited a total of 40.25% at 300-700^{0}C because of water and carbonate loss, in this the water loss takes place from dehyroxylation of the layers. Because of the lattice dehydroxylation removal of carbonates takes place.

SEM: The SEM image of Ca-Al-CO$_3$ with a metal ratio of 3:1 is shown in Figure (8). High crystallinity is exhibited in the image. Hexagonal shaped particles are seen along with big needle shaped particles.

Characterization of the product 3-Acetylcoumarin

FTIR spectrum of 3-acetylcoumarin (Fig. 9): FT- IR spectra of this compound provided a preliminary idea in the confirmation of the formation of product. According to the FT-IR, presence of peaks at 1627.29 cm^{-1} clearly indicated the utilization of starting materials and their transformation into the product.

The presence of carbonyl group in a compound generally gives rise to a band in the range of 1780–1700cm^{-1} (Smith, 1999 and Peesole, 1976). Hence, for 3AC the band at 1723 cm^{-1} in the spectrum is readily assigned to C=O group stretching vibrations present in coumarin ring (pyr-one). The band at 1686 cm^{-1} is assigned to carbonyl group (C=O) stretching vibrations present in acetyl group. The difference in the experimental frequencies between the two carbonyl groups is 47cm^{-1}, which is attributed to the conjugation effect. Further, the corresponding peaks at 2945, 1728.29, 1627.29, 1599.23, 1351,7 52 and 1157.28 cm^{-1} have been related to – Ar C-H str, C=O ester (str), C=O Exo cyclic ketone (str), C= C str. (Aromatic), C-C str. (exo cyclic), (C-H out plane bending) and (C-O str) respectively in the compound.

Mass Spectral Studies (Fig. 10)

NMR spectral studies: The NMR serves is a great resource in determining the structure of an organic compound by revealing the hydrogen and carbon skeleton. To furnish a definite assignment and analysis of 1H and ^{13}C NMR spectra of 3-AC, respectively has been analysed Proton NMR strongly revealed f the formation of the product by its δ value at 2.71, 7.32–7.65,

and 8.45ppm corresponding to the aliphatic C–H, Ar-H and Benzo fused coumarin-H protons of compound (Fig.11).
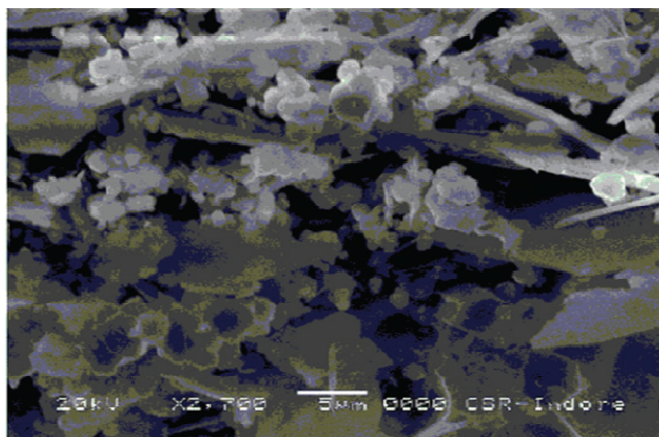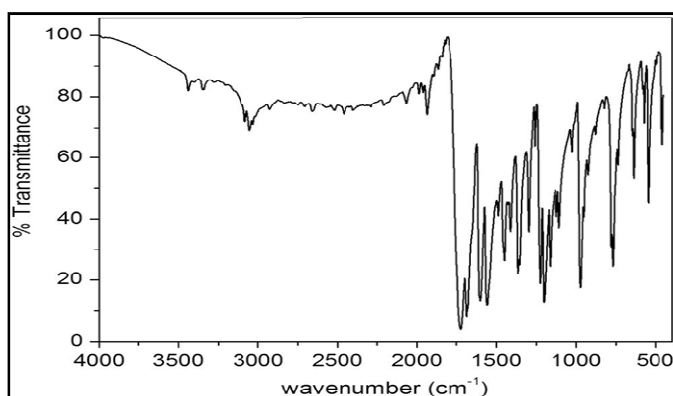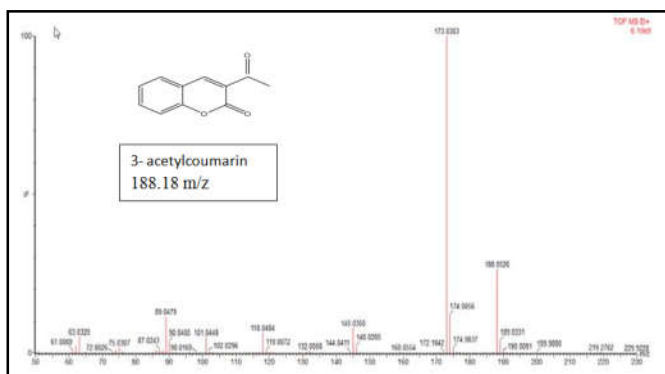
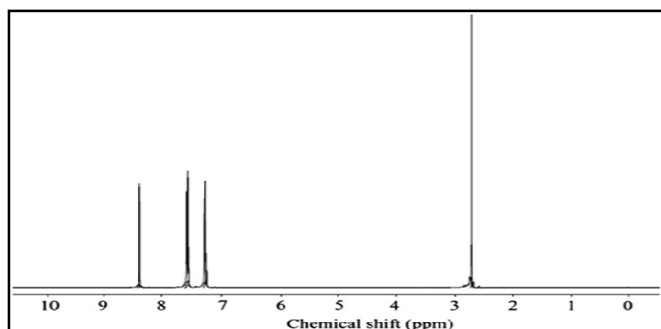

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11. Proton NMR spectrum of 3-acetylcoumarin

The experimental chemical shifts, isotropic shielding constants and the assignments are given in ^{13}C spectra (Fig 12). Aromatic carbons give signals with chemical shift values from 100 to 200 ppm (Kalinowski, 1988 and Pihlaja, 1994). The

experimental chemical shift of 3-AC occurs in the range of 116.61–195.39 ppm. The carbonyl carbon (C_{17}) chemical shift is observed at the downfield of 195.386 ppm. The methyl group carbon (C_{19}) shows a singlet peak at 30.493 ppm due to the electro-negative oxygen atom attached to adjacent carbon atom. Due to the presence of oxygen atom in pyrone ring, chemical shift of all carbons in heterocyclic ring are set downfield. Therefore C_2, C_{10}, C_4 chemical shift observe at the downfield of 159.146, 155.251, 147.395 ppm. The benzene ring carbon C_7, C_5, C_6, C_8, C_9 and C_3 chemical shift observe at 134.38, 130.23, 124.97, 124.47, 118.21 and 116.61 ppm. The peak observed at 77 ppm is due to solvent.
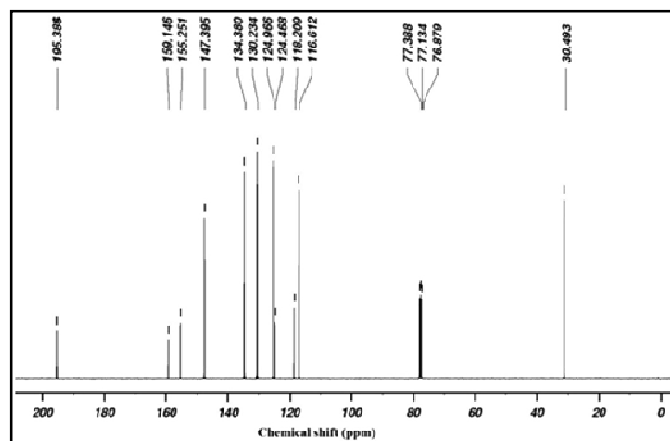

Fig. 12. ^{13}C NMR spectrum of 3-acetylcoumarin

Recyclability of the catalyst: At the end of the reaction, the catalyst was recovered by a simple filtration. The recycled catalyst was washed with de-ionized water, then filtered and dried and was further subjected to a second run for the reaction. The catalysts was weighted after filtration and before using and reusing for the next reaction. The results show that these catalysts are recyclable. The efficiency of Mg-Al hydrotalcite in synthesis of 3AC could be exhibited even after 6 cycles.

Conclusion

The synthesis of 3-acetylcoumarin was found to take place in water a green solvent. The use of Mg-Al-CO$_3$ and Ca-Al-CO$_3$ also are non toxic and environment friendly catalyst. The synthesis need lesser time. The proposed structures for these coumarines have been supported using FTIR, H^{1}NMR, ^{13}CNMR and Mass spectral techniques. The catalysts have been found to be recyclable.

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