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Role of basicity, calcinations, catalytic activity and recyclability of hydrotalcite in eco-friendly synthesis of coumarin derivatives

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ABSTRACT

An efficient and simple protocol is described for synthesis of coumarin derivatives using Mg–Al-CO_3 and Ca–Al-CO_3 hydrotalcite as an environmental friendly and reusable heterogeneous catalyst under solvent free conditions. The catalysts were characterized by Hammett titration, SEM and XRD data. Present study revealed that catalytic activity and basicity depend on compositions of hydrotalcite. The calcined hydrotalcite with an Mg/Al of 3:1 derived from calcinations at 750 K was found to be suitable catalyst that gives the highest basicity and the best catalytic activity for this reaction. Catalyst allows short reaction time, high catalytic activity, easy to work up and is reusable. Step economy, atom efficiency and solvent free conditions are some important salient features of this protocol.

1. Introduction

Coumarins (chomene-2-ones, benzopyran-2-ones) are naturally occurring classes of compound, which having variety of pharmacological activity dependent on the substitution patterns [1]. Coumarins core structure represents a highly privileged and biologically relevant molecular scaffold which occurs in many natural products. For example, autumnariol has been isolated from onions of *Eucomis autumnalis* Greab (Liliaceae) [2]. A number of related natural products, such as autumnariniol [3], alternariol [4], and altenuisol [5], have been isolated (Fig. 1) [6]. Recently several synthetic procedures for the preparation of coumarin derivatives have been reported using montmorillonite K-10 [7], zinc [8], indium (III) chloride [9], $TiCl_4$ [10], $ZrCl_4$ [11], sulfated zirconia [12], Lewis acidic chloroaluminate ionic liquid [13], bismuth nitrate [14], Wells–Dawson heteropolyacid [15], samarium (III) [16], PIDA/I_2-mediated [17], $InCl_3$ [18], $HClO_4$·SiO_2 [19], DMAP and Et_3N [20]. Literature survey demonstrated that reported methods have suffered drawbacks such as low yield, long duration, and used hazardous solvent such as organic solvent as compared to water, not reusable, higher catalyst loading, and relatively higher temperature conditions.

The drawback of ionic liquids is that it cannot be removed by distillation and their limited solubility in water restricts their use. They have high cost and also acute toxicity for aquatic organism and human [21]. Hydrotalcites (HTs) are synthetic or natural layered materials made of positively charged two-dimensional sheets of mixed hydroxides with water and exchangeable charge-compensating anions [22]. Hydrotalcites are increasingly regarded as a good alternative to the traditional homogenous base catalysts such as NaOH and KOH for several base-catalyzed reactions that are important for the pharmaceutical and fragrance industries [23]. A well-documented example is the isomerization of eugenol and safrole [24]. As far as green chemistry is concerned, hydrotalcites offer several advantages over these corrosive, dissolved catalysts, easy separation from the reaction mixture, recycling possibilities, decreased corrosion of the reactor, so forth [25]. The range of applications of hydrotalcite base materials is virtually unlimited. Hydrotalcites can be involved in the preparation of catalysts dedicated to the production of H_2 [26], wide range of organic compounds [27] and production of biodiesel by transesterification of triglycerides with methanol [28]. In addition to the above numerous experimental investigations have been published on the use of hydrotalcites for catalytic applications [29]. In present communication, we have used hydrotalcite as catalyst led to formation of high yield of coumarin derivatives under solvent free conditions.

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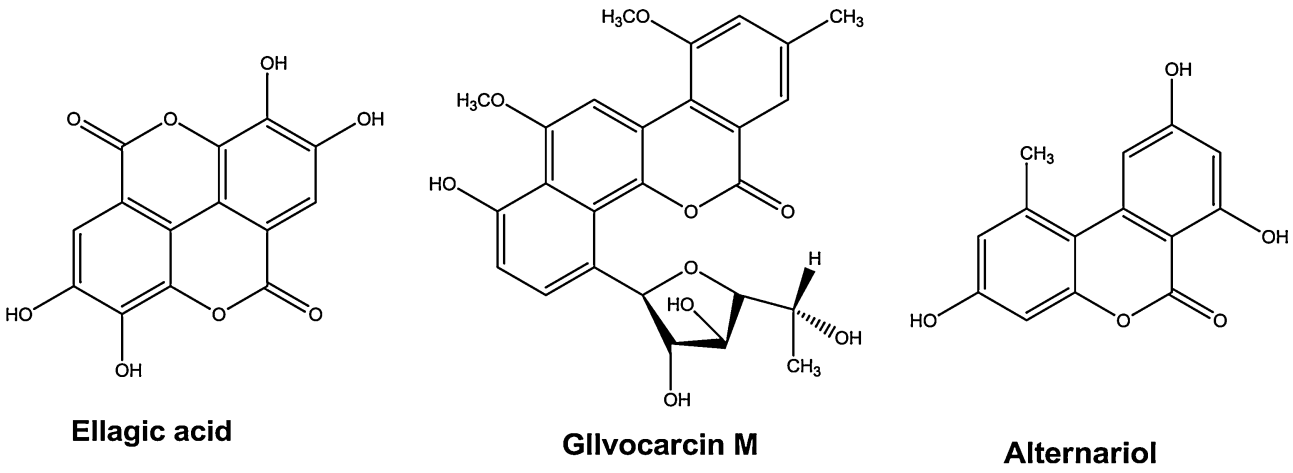

Fig. 1. Natural occurring products with coumarins core.

Table 1
Optimization of hydrotalcite as a catalyst (Mg–Al-HT (Mg/Al = 3)).

Entry	Catalyst loading (mg)	Time (min)	Yield (%)
1	10	120	52
2	20	90	74
3	50	30	97
4	75	30	97
5	100	30	96

2. Results and discussion

In order to evaluate the appropriate catalyst loading, a model reaction of resorcinol (0.0025 mol) and ethyl acetoacetate (0.0025 mol) were carried out using 10 mg, 20 mg, 50 mg, 80 mg, and 100 mg of hydrotalcite as catalyst at 70 °C. The catalyst loading 50 mg was found to be the optimal quantity (Table 1). Catalyst was reused and the results show that the hydrotalcite (Mg–Al-CO_3) can be reused as such without significant loss in yield (Table 2). Reusability of catalyst reduces the cost of production. The procedure was efficient and greatly reduced the role of solvent thus reducing environmental pollution. This procedure was easy to work up because after completion of the reaction, mass was cooled to room temperature and poured directly in cold water. Precipitate was form and filtered easily. Solid was dissolved in ethanol and filtered to separate hydrotalcite.

Basicity of hydrotalcite is a key for the preparation of material with high performance [30]. It can be achieved by changing the nature of M^{2+}/M^{3+} metals [31]. As far as Mg–Al mixed oxides of hydrotalcite is concerned, a correlation can be established between the composition and the basicity: when the amount of Al increases, the total number of basic sites decreases [25(a),32]. The decrease in basic site density observed in Mg–Al mixed oxide derived from hydrotalcites when increasing the Al content is reported to be the reason for decreasing activity in the Knoevenagel condensation reaction between glyceraldehydes acetonide and ethyl acetoacetate [33]. The performance of Mg–Al mixed oxide in the methanolysis of soybean oil was shown to be dependent on the Mg/Al ratio [34]. Numerous authors have tried to identify the best composition of Mg–Al mixed oxide catalysts in the case of various reaction. A set of Mg–Al hydrotalcite-like precursors with different Mg/Al atomic ratios was studied by Diez et al. [35]. The optimum Mg/Al molar ratio is dependent on the target reaction and more precisely, on the basic strength needed to activate the reactant. In order to check the basicity effect of hydrotalcite catalyst on the yield of the synthesized coumarin derivatives, hydrotalcite with different metallic ratios of Mg–Al-CO_3, Ca–Al-CO_3 and their metal oxide were tried under solvent free conditions and concluded that (3:1) Mg–Al-CO_3, (3:1) Ca–Al-CO_3 were more suited hydrotalcites to catalyze the reaction (Table 3). The results show that basicity of hydrotalcite affected the reaction time and yields of target product. Among all the metallic ratio of hydrotalcites, 3:1 ratio of hydrotalcite (Mg–Al-CO_3) gives the highest yield with lower time.

Table 2
Reusability of hydrotalcite (Mg–Al-HT, (Mg/Al = 3)).[a]

Product	Fresh HT	Reuse (I)	Reuse (II)	Reuse (III)	Reuse (IV)
1a	97	95	95	93	92

[a] Reaction conditions: resorcinol (0.0025 mol), ethyl acetoacetate (0.0025 mol), hydrotalcite (50 mg), heating at 70 °C.

2.1. Recyclability and reusability of hydrotalcite

A model reaction has been carried out using of resorcinol (0.0025 mol) and ethyl acetoacetate (0.0025 mol) for recyclability and reusability of hydrotalcite as catalyst by incorporating 50 mg of hydrotalcite catalyst. After completion of reaction, the contents were filtered to recycle the hydrotalcite catalyst through whatman filter 42. Recycled hydrotalcite washed with 5 mL ethanol to remove organic impurities if any. Mg^{II} hydrotalcite catalyst can be readily recovered and reused for at least four runs without any significant loss of activity. XRD data of recovered hydrotalcite (Fig. 2) which showed the similar profile as fresh catalyst which confirmed that layered structure of hydrotalcite was maintained after the reaction.

2.2. Catalytic activity of hydrotalcite

By exploring the synthesis of coumarin derivatives the catalytic activity has been observed, results are incorporated in Table 4.

Table 3
Effect of metal composition of hydrotalcite on yield of coumarin.[a]

Entry	Ratio of hydrotalcite	Time (min)	Yield (%)
1	(2:1) Mg–Al-CO_3	70	84
2	(3:1) Mg–Al-CO_3	30	97
3	(4:1) Mg–Al-CO_3	70	79
4	(2:1) Ca–Al-CO_3	80	74
5	(3:1) Ca–Al-CO_3	60	90
6	(4:1) Ca–Al-CO_3	90	78
7	MgO	150	21
8	CaO	180	15

[a] Reaction conditions: solvent free conditions, heating at 70 °C.