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Nano-sulfated zirconia as an efficient, recyclable and environmentally benign catalyst for one-pot three component synthesis of amidoalkyl naphthols

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Abstract

One pot synthesis of amidoalkyl naphthols by reaction of aromatic aldehydes, 2-naphthol and amide/urea using nano-sulfated zirconia as a catalyst is reported. The reaction was carried out under solvent-free conditions. The method gave good yields of amidoalkyl naphthols in short reaction time. The catalyst is recycled for five consecutive times without loss of activity.

Keywords: Amidoalkyl naphthol; Nano-sulfated zirconia; Solvent free; Multicomponent

One pot multicomponent reactions (MCRs) have attracted considerable interest owing to their exceptional synthetic efficiency. The structure of the reaction product can easily be diversified by systematic variation of each input. Moreover, the starting materials are either commercially available or easy to prepare [1]. Some examples of MCRs are Biginelli [2], Ugi [3], Passerini [4] and Mannich [5].

The 1-amidoalkyl-2-naphthol scaffolds are useful intermediates which can be easily converted into biologically active derivatives by amide hydrolysis [6,7]. Amidoalkyl naphthols can be prepared by condensation of aromatic aldehydes, β-naphthol and amides, urea or acetonitrile in the presence of a Lewis or Brønsted acid catalysts. Several methods have been documented in the literature for synthesis of these compounds such as montmorillonite K10 clay [8], $Ce(SO_4)_2$ [9], iodine [10], $K_5CoW_{12}–O_{40}\cdot 3H_2O$ [11], p-TSA [12], sulfamic acid [13], $HClO_4–SiO_2$ [14], ionic liquids [15], silica sulfuric acid [16], cation-exchanged resins [17], $Al(H_2PO_4)_3$ [18], $Fe(HSO_4)_3$ [19], $Yb(OTf)_3$ [20], wet cyanuric chloride [21], polymer-supported sulfonic acid [22], $FeCl_3–SiO_2$ [23], $ZrOCl_2$ [24], CuPMo [25], PPA-SiO_2 [26], VB1[27], TEBAC [28], $H_3Mo_{12}O_{40}P$ [29], indium(III) chloride [30], strontium(II) triflate [31], P_2O_5 [32], $H_4SiW_{12}O_{40}$ [33], TBBDA [34], trityl chloride [35], bismuth(III) nitrate pentahydrate [36], hexanesulphonic acid sodium [37], dual metal cyanide complex [38] and copper *o*-toluenesulfonate [39].

However, some of these protocols bear drawbacks such as long reaction time, use of toxic and expensive catalyst, carcinogenic solvent, unavailability and reusability of the catalyst. Therefore, there is still need for a green catalyst which can dominate one or more drawbacks and also an environmentally benign procedure to synthesize amidoalkyl naphthols.

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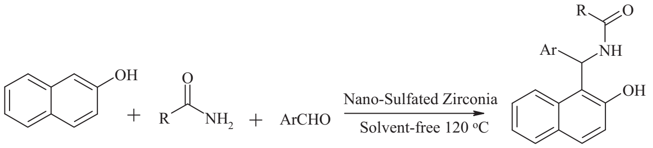

Scheme 1.

Solid heterogeneous catalyst is an active area of current research. Using solid acid catalyst has some advantages such as reduced equipment corrosion, ease of products separation, recycling of the catalyst and environmental acceptability as compared to homogeneous kind [40]. Sulfated zirconia is a well-known solid acid catalyst, which has been widely studied in terms of their catalyst properties and of their preparation methods [41]. To the best of our knowledge, the activity of sulfated zirconia for synthesis of amidoalkyl naphthols has not been studied.

In the present study, we report a general, efficient and green protocol for the synthesis of 1-amidoalkyl-2-naphthols by the 2-naphthol, aromatic aldehydes and amides/urea using nano-sulfated zirconia under solvent free conditions (Scheme 1).

1. Experimental

Chemicals were purchased from Fluka, Merck and Aldrich chemicals companies. The products were characterized by comparison of their spectral (IR, ^{1}H NMR), TLC and physical data with the authentic samples. Nano-sulfated zirconia was prepared according to the reported procedure [42].

1.1. General procedure

A mixture of 2-naphthol (5 mmol), aldehydes (5 mmol), and acetamide/urea (5.5 mmol) and nano-sulfated zirconia (0.2 g) was heated in an oil bath at 120 °C for specified time (Table 1). The reaction was followed by TLC and after completion of the reaction, the mass was cooled to 25 °C; and then the solid residue was dissolved in acetone and the mixture stirred for 5 min. The catalyst was recovered and washed with acetone followed by drying at 110 °C for 2 h and thermal activation at 450 °C (2 h). Then filtrate solution was evaporated under reduced pressure and the solid so obtained was recrystallized in aqueous ethanol. The desired pure product(s) was characterized by comparison of its physical data with those of known compounds.

Table 1
Nano-sulfated zirconia catalyzed synthesis of amidoalkyl naphthol derivatives.

Entry	Ar	R	Time (min)	Yield (%)	mp (°C)	
					Found	Reported
1	Ph	CH_3	32	91	240–242	241–243 [9]
2	2-Cl-C_6H_4	CH_3	90	83	193–195	194–196 [13]
3	4-Cl-C_6H_4	CH_3	35	92	225–227	224–227 [9]
4	4-Br-C_6H_4	CH_3	35	90	226–228	228–230 [8]
5	4-Me-C_6H_4	CH_3	80	88	215–216	214–216 [15c]
6	4-MeO-C_6H_4	CH_3	85	87	182–184	184–186 [9]
7	3-NO_2-C_6H_4	CH_3	35	93	237–238	238–240 [15c]
8	4-NO_2-C_6H_4	CH_3	32	93	247–249	248–250 [23]
9	4-CN-C_6H_4	CH_3	30	90	230–232	232–234 [15c]
10	Ph	NH_2	30	94	177–178	176–178 [15c]
11	4-Me-C_6H_4	NH_2	80	89	115–117	117–118 [31]
12	4-Cl-C_6H_4	NH_2	30	94	166–168	168–169 [17]
13	3-MeO-C_6H_4	NH_2	60	81	243–245	242–244 [33]
14	1-Naphthyl	NH_2	80	89	164–166	163–165 [10]
15	3-NO_2-C_6H_4	NH_2	40	92	191–193	192–193 [15c]
16	4-NO_2-C_6H_4	NH_2	35	91	164–166	163–165 [34]

2. Results and discussion

In the beginning, we decided to investigate the role of nano-sulfated zirconia as a catalyst in the synthesis of amidoalkyl naphthols (Scheme 1). In the absence of a catalyst no amidoalkyl naphthol was observed, even after a prolonged reaction time. The effect of the catalyst was also studied under various conditions. In all cases the amount of the catalyst was crucial to a good yield and reaction rate. It was determined that 0.2 g of the catalyst (nano-sulfated zirconia) was optimal to this reaction. If less than 0.1 g of nano-sulfated zirconia was used the low yields resulted, even after a long reaction time; the yield of the products did not increase when more than 0.2 g of nano-sulfated zirconia was used.

In all cases, aromatic aldehydes with substituents carrying either electro-donating or electron-withdrawing groups reacted successfully and gave the products in high yields. It was shown that the aromatic aldehydes with electron withdrawing groups reacted faster than the aromatic aldehydes with electron releasing group as would be expected. Aromatic aldehydes with steric hindrance such as 2-chloro benzaldehyde reacted at long reaction times. The high catalytic activity of nano-sulfated zirconia is due to high acidity and the large pore dimensions which provide good access to the acid sites on the surface of catalyst [41].

To study the regeneration and reusability of the catalyst, catalyst was recovered from the reaction mixture by filtration and washed with acetone followed by drying at 110 °C for 2 h and thermal activation at 450 °C for 2 h. Thus regenerated catalyst was used for the reaction synthesis of entry 1 under the similar reaction conditions for 5 cycles. After every reaction cycle the catalyst was recovered, washed and activated as above. The same activity as fresh catalyst without any loss of its activity for recovered catalyst was found.

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