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Aluminatesulfonic acid: Novel and recyclable nanocatalyst for efficient synthesis of aminoalkyl naphthols and amidoalkyl naphthols

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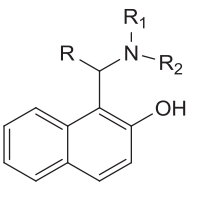
ABSTRACT

In this study, an efficient, mild, and eco-friendly procedure is developed for the preparation of 1-amidoalkyl-2-naphthols and Betti bases from one-pot three-component condensation of aldehydes, 2-naphthol, and nitrogen sources (amides for amidoalkyl naphthols and amine for Betti bases) in the presence of aluminatesulfonic acid nanoparticles (ASA NPs) as recoverable catalyst under solvent-free conditions. ASA NPs were prepared by a simple reaction of net chlorosulfonic acid and sodium aluminate in high purity. ASA NPs were characterized by Fourier transform IR, X-ray powder diffraction, transmission electron microscopy, energy-dispersive X-ray, thermal gravimetric analysis, and UV diffusion/reflectance techniques. On the basis of the thermal gravimetric analysis and some activation parameters evaluated from decomposition thermal steps using Coats–Redfern model, the catalyst showed high thermal stability. High yields, short reaction time, easy workup, inexpensive, and reusability of the catalyst are advantages of this method.

1. Introduction

Aminoalkyl naphthols (**1**, Betti bases) and amidoalkyl naphthols (**2**) with 1,3-amino-oxygenated functional group are considered as a class of biologically natural active products and potent drugs, which include many nucleosides, antibiotics, and human immunodeficiency virus protease inhibitors, such as lopinavir and ritonavir [1].



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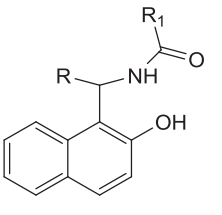

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Amidoalkyl naphthol can be easily converted to 1-(α-aminoalkyl) naphthol by amide hydrolysis reactions [2], which exhibits biological activities such as antibacterial, hypotensive, antipain, and bradycardia effects in humans [3–5].

In addition, 1-aminoalkyl alcohol type ligands have been used for asymmetric synthesis and as catalysts in some

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organic reactions [6]. They could act as chiral auxiliaries for the synthesis of α-aminophosphonic acids [7] and as chiral shift reagents for the preparation of carboxylic acids [5]. Moreover, because the amino and phenolic hydroxyl groups can be transformed into a wide variety of other functional groups, Betti base derivatives also provide convenient access to many of the useful synthetic building blocks [8]. 1-Amidoalkyl-2-naphthols and 1-(α-aminoalkyl)-2-naphthols can be converted to 1,3-oxazine and/or 1,3-oxazinone derivatives [9].

The chemistry of the Betti bases was introduced at the beginning of the 20th century by Mario Betti via a report on the synthesis of 1-(α-aminobenzyl)-2-naphthol [10]. The classical synthesis of Betti bases is generally a modified Mannich mechanism for condensation of 2-naphthol, aldehydes, and ammonia [11]. In fact, some modifications such as replacing of ammonia with other akylamines, quilinols, and naphthols can facilitate the process of preparation of Betti base derivatives [12]. Various methods are reported for synthesis of 1-amidoalkyl-2-naphthols and Betti bases; however, most of them either suffer longer reaction time or use catalysts that are nonrecoverable and user friendly [13]. Another approach for synthesis of Betti bases is hydrolysis of amidoalkyl naphthols. Therefore, synthesis of amidoalkyl naphthols seems to be important in this case. Recently, multicomponent condensation of aldehydes with β-naphthol and amide derivatives or acetonitrile has been reported as a practical synthetic route for the preparation of 1-amidoalkyl-2-naphthols [14].

Several Lewis and Brønsted acids, such as $SnCl_4 \cdot 5H_2O$ [15], polymer-supported sulfonic acid [16], ionic liquids [17], nano-sulfated zirconia [18], $[HMIM]C(CN)_3$ [19], $ZrO(OTf)_2$ [20], and $Bi(NO_3)_3 \cdot 5H_2O$ [21], have been applied to catalyze this transformation. Although these methods are quite useful, many of literature reports are associated with one or more limitations such as long reaction time, low yield, harsh reaction conditions, the use of corrosive, toxic, non-reusable, expensive, difficult-to-handle and large amount of catalysts, excess amount of acetamide (as reactant), and tedious workup procedures [13,17,22].

Hence, the development of clean processes and using eco-friendly catalysts with high catalytic activity and recoverability for the synthesis of 1-amidoalkyl 2-naphthols and 1-(α-aminoalkyl)-2-naphthols have been of interest under permanent attention.

One-pot catalytic transformation of organic compounds with readily available, nontoxic, and inexpensive reagents has attracted considerable attention because they are performed without isolating the intermediates reducing reaction time and saves both energy and raw materials [23]. Therefore, to find and develop new multicomponent reactions, researchers have made great attempts [17].

The development of clean technologies is of importance from a green chemistry point of view. The use of heterogeneous catalysts and replacing solution reaction with solvent-free ones are some cases that can help reduction of harmful effects of chemical reactions [24].

Nanocatalysts generally exhibit higher activity, greater stability, recycling potential, efficient recovery characteristics, and cost effectiveness, thereby they can be replaced with conventional catalyst [25,26].

In regard to mentioned points and the authors' research on the synthesis and applications of new heterogeneous nanocatalysts [27], in this work aluminatesulfonic acid nanoparticles (ASA NPs) were prepared via reaction between sodium aluminate and chlorosulfonic acid (1:1 mol ratio) (Scheme 1) [27d]. Afterward, its catalytic activity was evaluated by using multicomponent condensation reaction for the syntheses of 1-amidoalkyl-2-naphthols and 1-(α-aminoalkyl)-2-naphthols under solvent-free conditions (Scheme 2).

2. Experimental

All chemical reagents were purchased from Merck, Fluka, and Aldrich chemical companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC (eluent: EtOAc—*n*-hexane, 1:3). Nanostructure catalysts were characterized using a Philips X'Pert powder X-ray diffraction (XRD) diffractometer (Cu Kα radiation, $\lambda = 0.15406$ nm). Transmission electron microscopy (TEM) images were recorded using a Zeiss-EM10C operated at a 100 kV accelerating voltage. The thermogravimetric behaviors were obtained with STA 1500 °C (Rheo Metric Scientific). Energy-dispersive X-ray (EDAX) analyses were carried out on a PHILIPS XL30, operated at a 20 kV accelerating voltage. UV diffusion/reflectance spectra were recorded using a JASCO-V-670 spectrometer. Melting points were determined using a Barnstead Electrothermal (BI 9300) apparatus in open capillary tubes and all are uncorrected. IR spectra were obtained using a Fourier transform (FT) IR JASCO-680 spectrometer instrument using KBr discs. The ^1H NMR (400 MHz) and ^{13}C NMR (125 MHz) were run on a Bruker 400 MHz Ultrashield spectrometer (δ in ppm), using DMSO-d_6 as the solvent with TMS as internal standard.

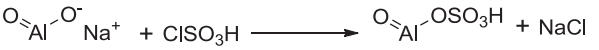
2.1. Preparation of aluminatesulfonic acid

To anhydrous sodium aluminate (0.1 mol, 8.2 g) in a three-necked round-bottom flask equipped with dropping funnel in an ice-bath, 0.1 mol (6.7 mL) chlorosulfonic acid was added dropwise with stirring. After completion, the reaction mixture was shaken for 1 h. The white solid was obtained after filtration and washing with cold ethanol, and then it was dried. After that, the product was poured into CCl_4 (100 mL) and was sonicated for 20 min to obtain 13.70 g (98%) of ASA NPs.

Mp >360 °C; IR (KBr, cm^{-1}): 3419, 3016, 2545, 1673, 1124, 946, 754, 700, 617.

2.2. General procedure for the preparation of 1-amidoalkyl-2-naphthols and 1-(α-aminoalkyl)-2-naphthols

In a round-bottom flask, the aldehydes (1 mmol), β-naphthol (1 mmol), nitrogen sources (1 mmol, amides and



Scheme 1. Synthesis of aluminatesulfonic acid nanoparticles.