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

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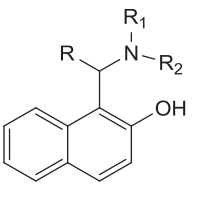
ABSTRACT

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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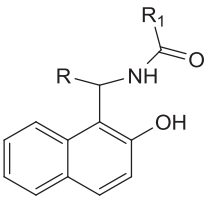

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Amidoalkyl naphthol can be easily converted to 1-(α-aminoalkyl) naphthol by amide hydrolysis reactions [2], which exhibits biological activities such as antibacterial, hypotensive, antipain, and bradycardia effects in humans [3–5].

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.

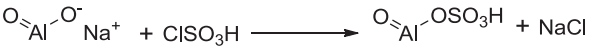
2.1. Preparation of aluminatesulfonic acid

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.

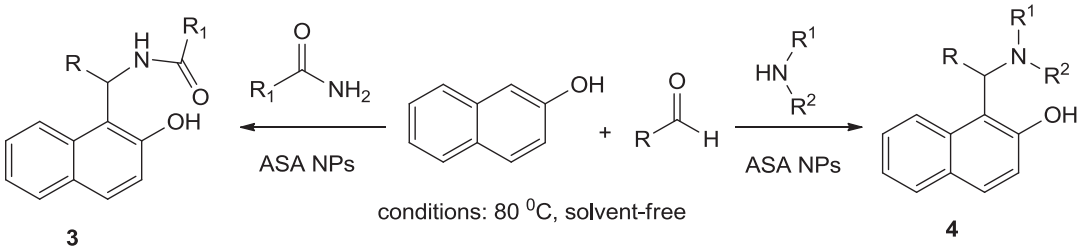
Mp >360 °C; IR (KBr, cm^{-1}): 3419, 3016, 2545, 1673, 1124, 946, 754, 700, 617.

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.



Scheme 2. Syntheses of 1-amidoalkyl-2-naphthols and 1-(α-aminoalkyl)-2-naphthols.

amine for amidoalkyl naphthols and aminoalkyl naphthol, respectively), and ASA NPs (0.1 mmol) were mixed thoroughly. The flask was heated at 80 °C with concomitant stirring. The reaction was monitored by thin-layer chromatography (*n*-hexane–EtOAc, 3:1). After completion of the reaction, hot ethanol (5 mL) was added and the obtained mixture was filtered and then washed with ethanol to separate the pure catalyst. The solvent was then evaporated and the crude products were recrystallized in ethanol to give pure products. The recovered catalyst was dried and reused for subsequent runs. The following is the physical and spectral data of new compounds.

2.2.1. N-*[5-Bromo-2-hydroxyphenyl)(2-hydroxynaphthalen-1-yl)methyl]acetamide (**3g**)*

Mp: 220–221 °C, R_f = 0.5 (*n*-hexane–ethyl acetate, 2:1); IR (KBr, cm^{-1}): 3501, 3424, 3160, 2977, 1654, 1519, 1440, 1415, 1367, 1328, 1270, 1170, 821, 811; ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm): 1.93 (s, 3H, CH_3), 6.68 (d, 1H, J = 8.8 Hz, CH), 7.14–7.21 (m, 3H, ArH), 7.28 (t, 1H, J = 7.4 Hz, ArH), 7.45 (t, 1H, J = 7.6 Hz, ArH), 7.61 (s, 1H, NH), 7.72 (d, 1H, J = 8.8 Hz, ArH), 7.78 (d, 1H, J = 8.0 Hz, ArH), 8.21 (d, 1H, J = 8.8 Hz, ArH), 8.46 (d, 1H, J = 8.8, ArH), 9.74 (br s, 1H, OH), 9.93 (br s, 1H, OH); ^{13}C NMR (125 MHz, DMSO-d_6) δ(ppm): 23.09, 56.58, 110.10, 117.40, 118.98, 119.16, 122.77, 123.73, 126.50, 128.62, 128.79, 129.39, 130.40, 131.69, 131.83, 133.12, 153.77, 154.36, 169.16.

2.2.2. N-*[(3-Ethoxy-4-hydroxyphenyl)(2-hydroxynaphtalene-1-yl)methyl]benzamide (**3l**)*

Mp: 225–228 °C; R_f = 0.41 (*n*-hexane–ethyl acetate, 3:1); IR (KBr, cm^{-1}): 3399, 3150, 2981, 1621, 1598, 1575, 1509, 1477, 1434, 1384, 1348, 1280, 1232, 1124, 813, 788, 777, 750; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 1.25 (t, 3H, J = 7.0 Hz, CH_3), 3.91 (q, 2H, J = 6.9 Hz, CH_2), 6.65–6.70 (m, 2H, ArH), 6.95 (s, 1H, CH), 7.21 (d, 1H, J = 7.2 Hz, ArH), 7.26 (d, 1H, J = 8.8 Hz, ArH), 7.32 (t, 1H, J = 7.4 Hz, ArH), 7.46–7.51 (m, 3H, ArH), 7.53–7.57 (m, 1H, ArH), 7.78–7.86 (m, 4H, ArH), 8.10 (d, 1H, J = 8.4 Hz, ArH), 8.83 (s, 1H, NH), 9.04 (br s, 1H, J = 8.4 Hz, OH), 10.35 (br s, 1H, OH); ^{13}C NMR (125 MHz, DMSO-d_6) δ(ppm): 15.19, 49.74, 64.43, 111.03, 113.40, 115.71, 119.05, 119.21, 119.90, 123.13, 123.32, 127.09, 127.55, 128.84, 129.00, 129.05, 129.61, 131.84, 132.74, 133.16, 134.96, 134.99, 146.30, 146.88, 153.47, 165.98.

*2.2.3. [(3-Bromophenyl)(2-hydroxynaphtalene-1-yl)methyl] urea (**3q**)*

Mp: 228–232 °C, R_f = 0.31(*n*-hexane–ethyl acetate, 3:2); IR (KBr, cm^{-1}): 3440, 3262, 2923, 1749, 1708, 1633, 1517, 1473, 1394, 1349, 1222, 1187, 1172, 1110, 1058, 993, 925, 838, 811; ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm): 6.28 (s, 2H, NH_2), 7.22 (d, 1H, J = 8.0 Hz, CH), 7.30 (t, 1H, J = 7.8 Hz, ArH), 7.41 (d, 1H, J = 9.2 Hz, ArH), 7.46–7.55 (m, 4H, ArH), 7.62 (s, 1H, ArH), 7.84 (d, 1H, J = 8.4 Hz, ArH), 7.98 (d, 1H, J = 8.0 Hz, ArH), 8.04 (d, 1H, J = 9.2 Hz, ArH), 8.94 (d, 1H, J = 2.8 Hz, NH), 9.43 (s, 1H, OH); ^{13}C NMR (125 MHz, DMSO-d_6) δ(ppm): 53.40, 113.77, 117.37, 122.48, 123.52, 125.72, 126.34, 128.04, 129.18, 129.25, 130.40, 130.90, 131.03, 131.45, 131.81, 145.82, 148.03, 149.56.

*2.2.4. 1-[(4-Methoxyphenyl)(morpholino)methyl]naphthalen-2-ol (**4c**)*

Mp: 131–133 °C, R_f = 0.56 (*n*-hexane–ethyl acetate, 1:1); IR (KBr, cm^{-1}): 3448, 2958, 2923, 2854, 2823, 1621, 1598, 1581, 1509, 1461, 1448, 1413, 1398, 1361, 1313, 1278, 1255, 1240, 1178, 1118, 1093, 1072, 1031, 998, 948, 877, 835, 821, 767, 746; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 2.40 (bt, 4H, J = 4.8 Hz, NCH_2), 3.62 (bs, 4H, OCH_2), 3.68 (s, 3H, OCH_3), 5.33 (s, 1H, CH), 6.87 (d, 2H, J = 8.8 Hz, ArH), 7.11 (dd, 2H, J_1 = 8.8 Hz, J_2 = 2.0 Hz, ArH), 7.26 (t, 1H, J = 7.4 Hz, ArH), 7.41 (dd, 1H, J_1 = 8.4 Hz, J_2 = 6.8 Hz, ArH), 7.54 (d, 2H, J = 8.4 Hz, ArH), 7.73 (d, 1H, J = 8.8 Hz, ArH), 7.77 (d, 1H, J = 8.0 Hz, ArH), 8.03 (br s, 1H, OH); ^{13}C NMR (125 MHz, DMSO-d_6) δ(ppm): 52.44, 55.44, 66.62, 69.81, 114.57, 116.42, 119.88, 122.03, 123.00, 126.93, 128.79, 129.09, 129.64, 131.62, 132.50, 154.55, 154.87, 159.24.

3. Results and discussion

3.1. Characterization of ASA NPs

Some techniques such as IR spectroscopy, thermal gravimetric analysis (TGA), powder XRD, EDAX spectroscopy, and TEM were used to characterize ASA NPs.

Some important changes in the structure of molecular species were confirmed by FTIR spectroscopy. In the IR spectra of anhydrous sodium aluminate (Fig. 1a) the bands at 3550–3238 and 1671 cm^{-1} are attributed to the vibrational bending mode of –OH group of physically adsorbed water. The intensity of broad band at 1452 cm^{-1} corresponding to the carbonate increased after exposing to the air [28]. The band at 825 cm^{-1} is corresponded to the formation of O–O triangular species bonds, and the band at 460 cm^{-1} is attributed to O–Na–O bonds [28]. The bands located at 644, 615, 580, and 534 cm^{-1} have been associated with the vibrations of Al–O bond [29].

The broad peaks at 3419–2545 and 1673 cm^{-1} in the IR spectrum of aluminatesulfonic acid (Fig. 1b) are attributed

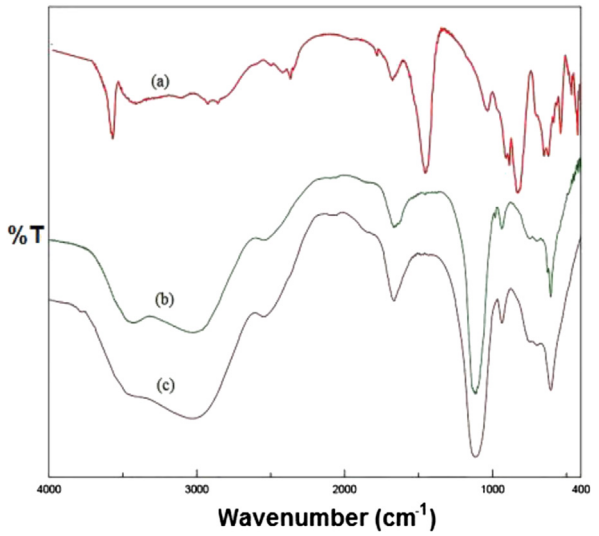


Fig. 1. FTIR spectra of (a) sodium aluminate; (b) fresh aluminatesulfonic acid; and (c) used aluminatesulfonic acid.

to the stretching and bending vibrations of −OH groups, respectively. The broad peaks at 1124 and 946 cm^{-1} are assigned to stretching vibration of S−OH and asymmetric stretching vibration of S═O of the sulfonic acid bonds. The signals appeared at 754, 700, and 617 cm^{-1} are related to Al═O and Al−O stretching vibrations.

The XRD technique was used to describe the crystalline structure of the nanocompounds. Many prominent Bragg reflections reveal the resultant particles of $NaAlO_2$ with an orthorhombic structure [30].

The crystalline structure of aluminatesulfonic acid was analyzed by XRD (Fig. 2a). A small difference in the XRD patterns between $NaAlO_2$ and ASA NPs suggests that chemical reaction does not affect the microstructure of sodium aluminate. The size of the ASA NPs was determined from X-ray line broadening by using the Debye−Scherrer formula ($D = 0.9\lambda/\beta \cos\theta$). For the (022) reflection signal, the average size of the ASA NPs was estimated to be around 33 nm.

Furthermore, the formation of expected sulfated catalyst was also confirmed by EDAX spectroscopy (Fig. 3). EDAX analysis showed the presence of sulfur, oxygen, and aluminum in the ASA nanocatalyst. The elemental distribution mapping of this analysis shows signals of oxygen−aluminum−sulfur in the ratio of 56.9:20.0:23.2 wt %, respectively (Table 1).

TEM of ASA NPs (Fig. 4) clearly shows that nanoparticles are almost spheroidal with diameters in the range of 15−60 nm with a mean size of 32 nm, which is near to average particle size obtained from XRD pattern. No pore formation was observed in TEM analysis; thus, it is suggested that reactions take place on the surface of a catalyst.

The thermal stability of ASA NPs was studied by TGA. TGA diagram of ASA NPs was recorded up to 1000 °C under nitrogen atmosphere at a heating rate of 10 °C/min. The TG diagram of ASA NPs has been illustrated in Fig. 5. The first mass loss less than 200 °C is assigned to the removal of hydrated water molecules. In the second and third thermal decomposition steps, the catalyst loses about 9 and 17% of its weight assigned to decomposition of catalyst structure may be attributed to the removal of sulfur containing gases. Moreover, some activation parameters of thermal decomposition steps were evaluated based on the Coats−Redfern equation [31], and the results are compiled in Table 2. Relatively, high values of activation energy of decomposition confirm stability of the catalyst. The positive values of enthalpy change and Gibbs free energy indicate the endothermic character of decomposition processes. The negative values of entropy change suggest low rate of decomposition process of the current catalyst.

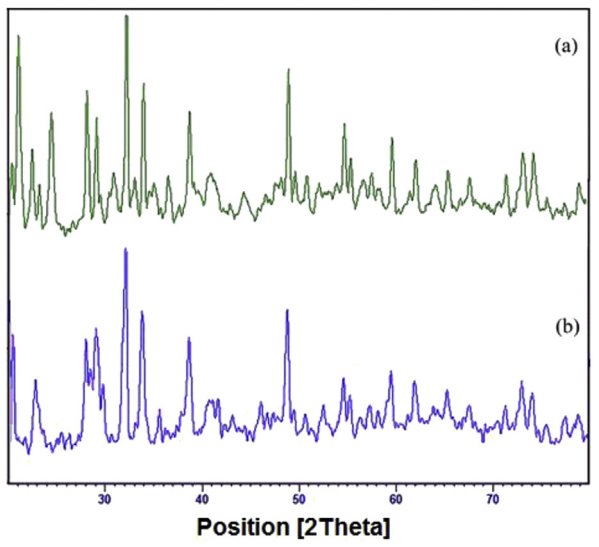


Fig. 2. Powder XRD pattern of the (a) ASA NPs and (b) reused ASA.

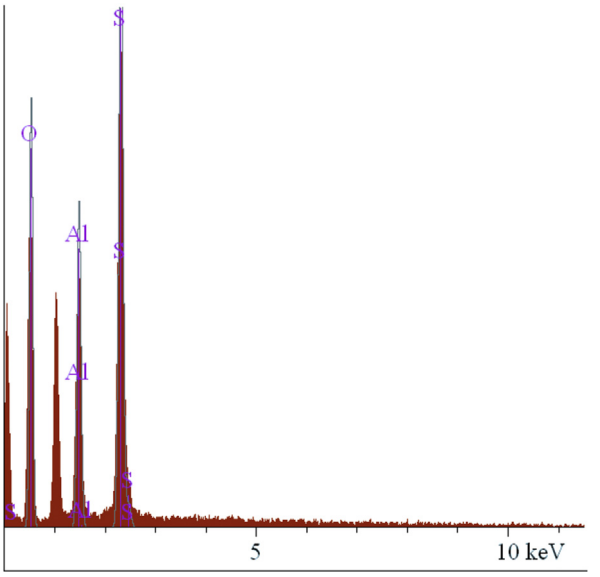


Fig. 3. EDAX spectroscopy pattern of ASA NPs.

Table 1
The elemental distribution of ASA NPs.

Elt.	Line	Intensity (counts/s)	Atomic%	Concentration	Units	
O	Ka	275.18	71.15	56.88	wt %	
Al	Ka	241.39	14.62	19.96	wt %	
S	Ka	492.06	14.23	23.16	wt %	
			100.00	100.00	wt %	Total

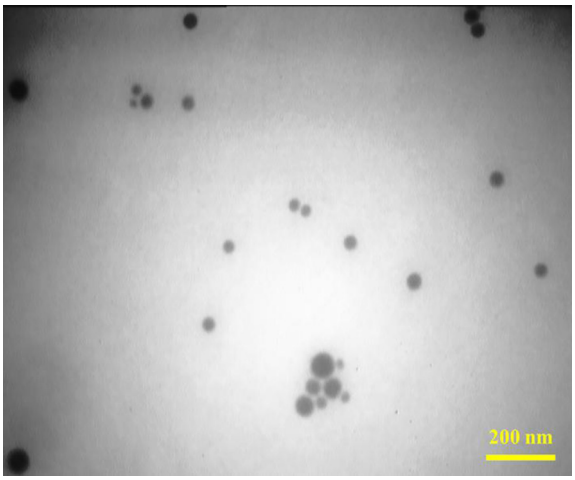


Fig. 4. TEM image of the ASA NPs.

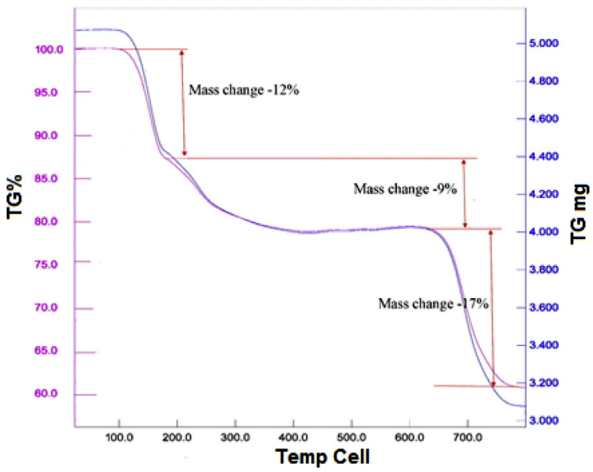


Fig. 5. TGA of the ASA nanocatalyst.

UV diffusion/reflectance spectra of ASA NPs (fresh and reused catalysts) are indicated in Fig. 6. Both fresh and reused catalysts show four absorption bands in the range of 200–600 nm at 209, 259, 334, 397, and 490 nm wavelengths. The similarity between two spectra confirms retention of catalyst structure during the reaction pathway.

3.2. Catalytic investigations

The catalytic activity of the ASA NPs was assessed by using the ASA for the synthesis of pharmaceutically important amidoalkyl naphthol and aminoalkyl naphthol derivatives. The influences of reaction parameters such as the role of the solvent, amount of catalyst, and reaction temperature were investigated to optimize the reaction conditions (Table 3).

Initially, to compare the results between solvent and solvent-free conditions, the condensation of benzaldehyde (1 mmol), 2-naphthol (1 mmol), and acetamide (1.2 mmol) in the presence of ASA NPs (10 mol %) as a model reaction in different solvents was studied.

Among the tested solvents such as water, ethanol, chloroform, acetonitrile, and a solvent-free system, the excellent yield was obtained after 20 min for solvent-free conditions (Table 3, entries 4, 6–9).

Thereafter, investigating the effect of various amounts of ASA on the titled reaction was planned. For this mean, a typical reaction without any catalyst was carried out. It was found that only a trace amount of product was obtained in the absence of the catalyst even after prolonged reaction

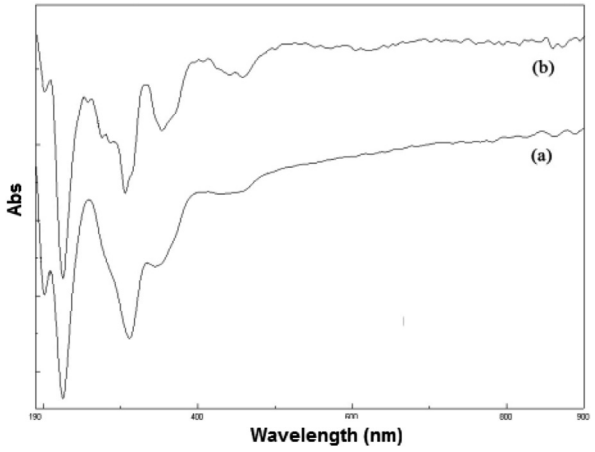


Fig. 6. UV diffusion/reflectance spectrum of (a) fresh and (b) reused catalysts.

Table 2
Thermal analysis data including temperature range, differential thermal gravimetry peak, and mass loss thermokinetic parameters of the thermal decomposition process.

Compound	Temperature range (°C)	Mass loss (%)	Peak temperature (°C)	E^* (kJ/mol)	A^* (1/S)	ΔS^* (kJ/mol K)	ΔH^* (kJ/mol)	ΔG^* (kJ/mol)
$AlHO_5S$	90–170	11.54	150.77	99.182196	7.54×10^9	-5.88×10^1	95.6577247	1.21×10^2
	170–385	9.55	229.02	15.872981	7.11×10^{-2}	-2.71×10^2	11.6979393	1.48×10^2
	385–755		688.54	147.27982	1.99×10^5	1.53×10^2	139.284326	2.87×10^2

Table 3
Catalytic activity evaluation and the effect of temperature and solvent for the synthesis of *N*-[(2-hydroxynaphthalen-1-yl)(phenyl)methyl] acetamide.

Entry	Catalyst (mol %)	Temperature (°C)	Solvent	Time	Yield[a] (%)
1	0	80	–	10 h	Trace
2	2.5	80	–	50 min	73
3	5	80	–	20 min	90
4	**10**	**80**	–	10 min	**96**
5	15	80	–	15 min	89
6	10	Reflux	H_2O	12 h	38
7	10	Reflux	EtOH	12 h	<10
8	10	Reflux	$CHCl_3$	12 h	20
9	10	Reflux	CH_3CN	12 h	<10
10	10	RT	–	150 min	Trace
11	10	40	–	93 min	52
12	10	60	–	61 min	69
13	10	70	–	40 min	86
14	10	100	–	10 min	87

The values related to the optimized reaction condition are represented in bold.
[a] Isolated yield.

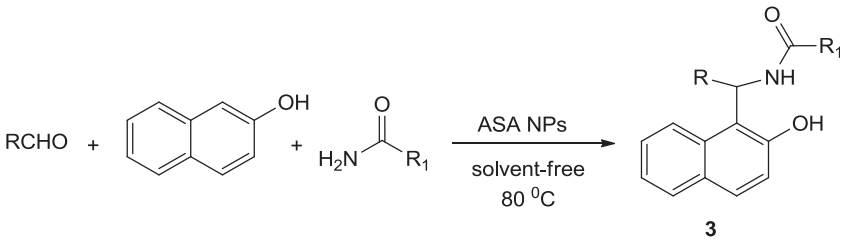
time (10 h). A quantitatively increase in catalyst amount of ASA from 2.5 to 10 mol % increased the reaction yield from 73 to 96% (Table 3, entries 2–4). The results showed that 10 mol % of catalyst led to the best yield in the shortest time. A higher loading of the catalyst amount (15 mol %) has no effect on the reaction yield (Table 3, entry 5).

After optimization of catalyst amount and solvent, the effect of temperature was studied. The results indicated that on raising the temperature from room temperature to 80 °C the reaction with increased yields occurs. The lower product yield was observed at a higher temperature (entries 10–14). In continuation to this study, the reaction was performed by using different quantities of reagents. The best result was obtained with a 1:1:1 ratio for benzaldehyde–2-naphthol–acetamide, respectively.

Using these optimized reaction conditions and for testing the general application of this catalyst, a variety of amidoalkyl naphthols and aminoalkyl naphthols were prepared by using various aldehydes, amides or amines, and β-naphthol. The results have been summarized in Tables 4 and 5.

In all cases, amidoalkyl naphthols and aminoalkyl naphthols were found as the sole products and no byproduct was observed. Aromatic aldehydes containing either electron-donating or electron-withdrawing groups reacted successfully and gave the products in excellent yields. However, as it is reported [19,42], using aromatic aldehydes with electron-withdrawing groups for the synthesis of amidoalkyl naphthols the reaction time was shorter than those with electron-donating groups. A suggested mechanism for the formation of amidoalkyl naphthol is depicted in Scheme 3, which is supported by the literature [15,17,43,44]. The reaction of β-naphthol with aromatic aldehydes in the presence of acid catalyst is known to give ortho-quinone methides (*o*-QMs). The same *o*-QMs generated in situ have been reacted with acetamide via conjugated addition on the α,β-unsaturated carbonyl

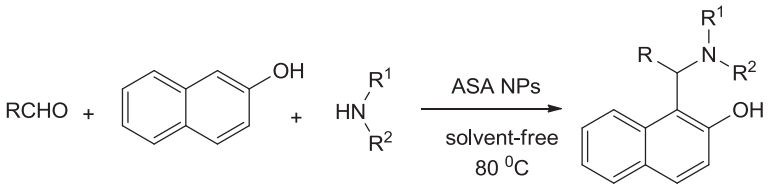
Table 4
The solvent-free synthesis of 1-amidoalkyl-2-naphthols in the presence of ASA NPs.[a]



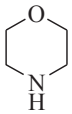
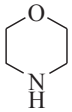
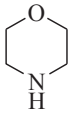
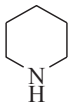
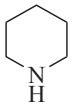
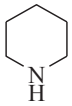
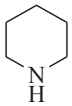
Entry	R	R_1	Product	Time (min)	Yield[b] (%)	Mp[c] (°C) [32–41]
1	C_6H_5	Me	**3a**	10	96	248–250
2	2,4-Cl–C_6H_3	Me	**3b**	9	94	230–232
3	3-Br–C_6H_4	Me	**3c**	10	95	210–213
4	4-NO_2–C_6H_4	Me	**3d**	8	95	246–249
5	C_6H_4–CH=CH	Me	**3e**	20	89	184–185
6	4-CHO–C_6H_4	Me	**3f**	30	91	235–237
7	5-Br-2-OH–C_6H_3	Me	**3g**	20	93	220–221
8	C_5H_4N	Me	**3h**	15	90	193–195
9	4-Me–C_6H_4	Ph	**3i**	12	92	220–222
10	C_2H_5	Ph	**3j**	30	67	243–245
11	4-NO_2–C_6H_4	Ph	**3k**	10	92	228–230
12	3-OEt-4-OH–C_6H_3	Ph	**3l**	19	90	225–228
13	2-Cl–C_6H_4	Ph	**3m**	10	92	270–272
14	4-NO_2–C_6H_4	NH_2	**3n**	10	96	160–162
15	4-OH–C_6H_4	NH_2	**3o**	17	86	151–153
16	4-OMe–C_6H_4	NH_2	**3p**	24	93	178–180
17	3-Br–C_6H_4	NH_2	**3q**	11	95	228–232

[a] Reaction conditions: aldehyde = 1 mmol; 2-naphthol = 1 mmol; amide = 1 mmol; ASA NPs = 10 mol %.
[b] Isolated yield.
[c] Melting points are uncorrected.

Table 5
Synthesis of 1-(α-aminoalkyl)-2-naphthol derivatives in the presence of ASA NPs.[a]



4

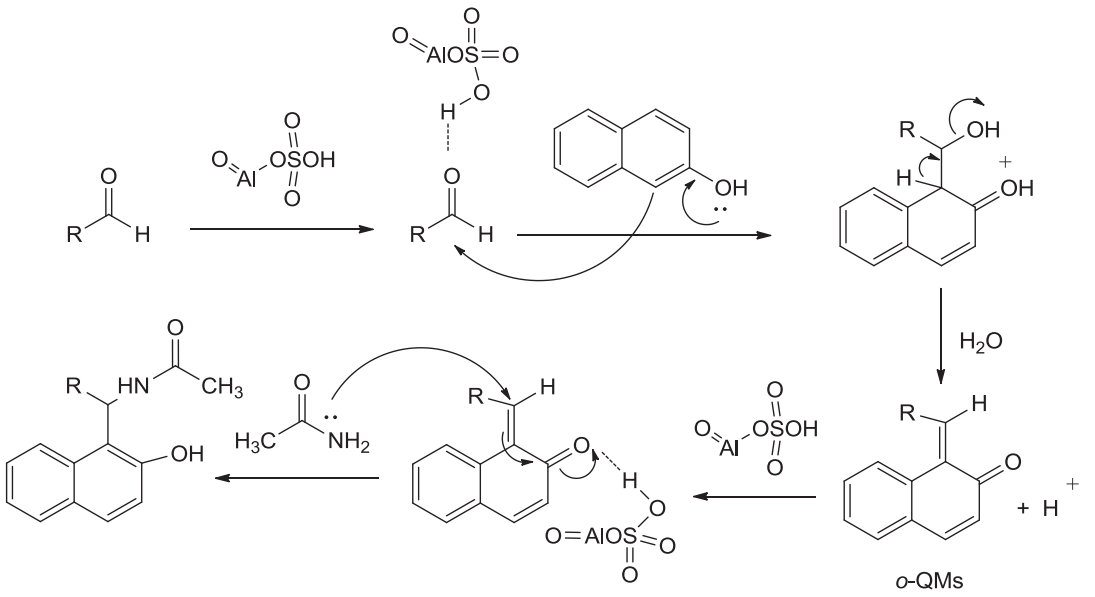
Entry	R	Amine	Product	Time (min)	Yield[b] (%)	Mp[c] (°C) [42]
1	C_6H_5		**4a**	15	92	175–177
2	4-Br–C_6H_4		**4b**	19	94	183–186
3	4-OMe–C_6H_4		**4c**	10	95	131–133
4	2-Thienyl		**4d**	20	88	189–190
5	4-Cl–C_6H_4		**4e**	24	92	143–145
6	4-NO_2–C_6H_4		**4f**	19	95	178–180
7	4-Br–C_6H_4		**4g**	23	92	165–167
8	4-ClC_6H_4	H_3CNHCH_3	**4h**	20	90	129–131
9	C_6H_5	$C_4H_9NH_2$	**4i**	18	92	134–136

[a] Reaction conditions: aldehyde = 1 mmol; 2-naphthol = 1 mmol; amide = 1 mmol; ASA NPs = 10 mol %.
[b] Isolated yield.
[c] Melting points are uncorrected.

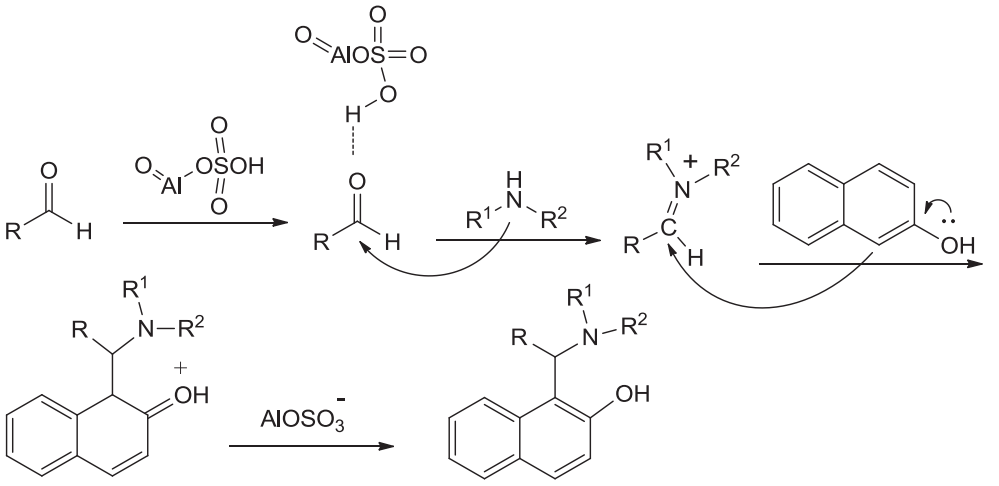
group to form 1-amidoalkyl-2-naphthol derivatives. The electron-withdrawing groups substituted on benzaldehyde in *o*-QM intermediate increase the rate of 1,4-nucleophilic (Michael) addition reaction because of alkene LUMO (a carbonyl group as in *o*-QM intermediate), which is at lower energy in the neighboring withdrawing groups compared with electron-donating groups [43,45]. A possible mechanism for the catalytic synthesis of aminoalkyl naphthols is expected on the basis of the reported literature [5,46]. It is assumed that the reaction proceeds via an iminium salt intermediate, which is generated by the condensation of an amine with aldehyde followed by the nucleophilic attack of 2-naphthol carbon on iminium carbon (Scheme 4).

Aliphatic aldehydes gave the products with lower yield compared with aromatic aldehydes in accordance with the previous reports that had used known catalysts, such as $FeCl_3{\cdot}SiO_2$ [33], H_3BO_3 [47], $H_4SiW_{12}O_{40}$ [48], probably because of less stability of an *o*-QM intermediate from aliphatic aldehydes.

No thioamidoalkyl naphthol product was obtained when thiourea was replaced with urea even after 10 h of



Scheme 3. The proposed mechanism for synthesis of 1-amidoalkyl-2-naphthols.



Scheme 4. The plausible mechanism for synthesis of 1-aminoalkyl-2-naphthols.

vigorous stirring, and a sticky mixture of reactant was obtained.

3.3. Recovering and reusing of the catalysts

The reusability is one of the important characteristics of heterogeneous catalyst. The recyclability of ASA was investigated for the model reaction of benzaldehyde, acetamide, and β-naphthol. Right after completion of reaction, the separated catalyst could be reused after washing with ethanol and drying at 100 °C for 2 h. This recycled catalyst was used for the subsequent catalytic runs. The catalytic system worked well up to five catalytic runs (Fig. 7).

The XRD pattern of the used ASA catalyst in the synthesis of *N*-[(2-hydroxynaphthalen-1-yl)(phenyl)methyl] acetamide is presented in Fig. 2b. As it is shown in figures, both fresh catalyst (Fig. 2a) and that recovered after use exhibited similar XRD patterns (Fig. 2b), which indicated that the structural properties of the catalyst were not affected during the reaction pathway.

IR and UV diffusion/reflectance spectra of catalyst before and after reaction are shown in Figs. 1 and 6, respectively. The IR peaks appeared at reused catalyst spectrum are well in agreement with those obtained for fresh catalyst. In addition, UV diffusion/reflectance spectrum of fresh catalyst shows four absorption bands similar to the appeared electronic transition bands in the used catalyst spectrum, suggesting no notable change in catalyst molecular structure.

To rule out the contribution of homogeneous catalysis, the standard leaching experiment was conducted. A model reaction in refluxing chloroform was proceeded for 6 h in the presence of catalyst, and then catalyst was removed by

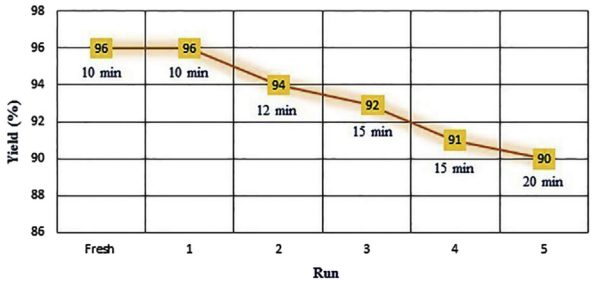


Fig. 7. Recovery and reusability of ASA NPs in the synthesis of *N*-[(2-hydroxynaphthalen-1-yl)(phenyl)methyl]acetamide.

filtration. The reaction was allowed to proceed without catalyst. There was no change in the progress of the reaction even after 10 h, indicating that no leaching has occurred; hence, no homogeneous catalyst was involved. Therefore, it seems that poisoning of some active sites of catalyst may be a reason for deactivation of it.

4. Conclusions

In this study, the synthesis and catalytic application of ASA NPs in the preparation of amidoalkyl naphthol and aminoalkyl naphthol are described. The reaction system was significantly affected by catalyst loading, reaction temperature, and solvent. In addition, it was found that the performance of the catalytic system greatly improved when it was used without solvents and it is important from the green chemistry point of view. The catalyst illustrated high efficiency and reactivity for the synthesis of amidoalkyl and aminoalkyl naphthol derivatives by using a variety of activated and deactivated aldehydes, amides or amines, and β-naphthol under solvent-free conditions. In addition, the catalyst could be recovered and reused at least five times without decreasing in activity and selectivity. Moreover, according to the XRD and FTIR spectra of the reused catalyst, the structure of ASA was not affected by the reaction medium and conditions. Therefore, the attractive features of this protocol are simplicity of the procedure, short reaction times, high yields, simple workup, inexpensive and reusable catalyst, and simple purification of the products.

Acknowledgment

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