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Research Article

Synthesis of 1-amidoalkyl-2-naphthol derivatives using Supported sulfonic acid on silica coated cobalt ferrite nanoparticles as a catalyst under solvent free conditions

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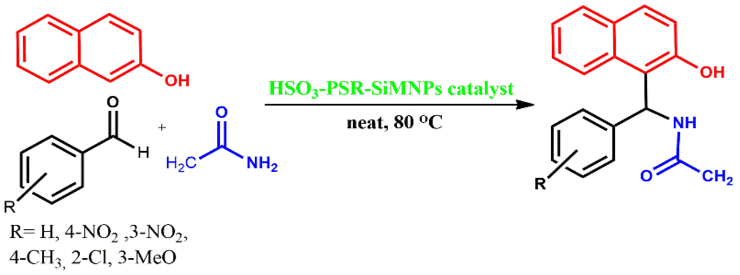
ABSTRACT

Anchored sulfonic acid on the surface of a silica-coated cobalt ferrite core was efficiently applied in the one-pot preparation of 1-amidoalkyl-2-naphthols under solvent-free conditions at 80 oC. The catalyst is readily recovered by simple magnetic decantation and can be recycled 10 times with no significant loss of catalytic activity

Keywords: Cobalt ferrite, 1-amidoalkyl-2-naphthols, magnetic nanoparticles, sulfonic acid

1. Introduction

One-pot multicomponent reactions (MCRs) have become a promising synthesis procedure in recent years because of the single operation without isolating the intermediates as well as reducing the reaction times and energy consumption [1-2]. The synthesis of 1-aminoalkyl-2-naphthol derivatives is one of the classic MCRs as these compounds can be easily converted to biologically active derivatives for different biological applications such as antitumor, antibiotic, analgesic, antihypertensive and anticonvulsant agents [3]. There have been efforts made by researchers for developing MCRs to prepare the 1-aminoalkyl-2-naphthols from aldehydes under the sonication conditions or heating [4]. However, some of these procedures and synthesis strategies are harmful to the environment and have limitations including high reaction temperature, toxicity, prolonged reaction time, and lower efficiency in obtaining the target product [5]. The demand for environmentally benign procedure with heterogeneous and reusable catalyst promoted us to develop a safe alternate method for the preparation of 1-aminoalkyl-2-naphthol derivatives. In pursuit of this goal, we wish to explore a straightforward synthesis of 1-aminoalkyl-2-naphthol derivatives via the one-pot three-component reaction under solvent-free conditions using a sulfonic acid moiety grafted on the surface of silica-coated cobalt ferrite ($CoFe_2O_4@SiO_2$-$RSRSO_3H$) as an efficient magnetic powerful solid acid catalyst with good stability (Scheme 1).



Scheme1. HSO_3-RSR-SiMNPs catalyzed synthesis of 1-aminoalkyl-2-naphthol derivatives

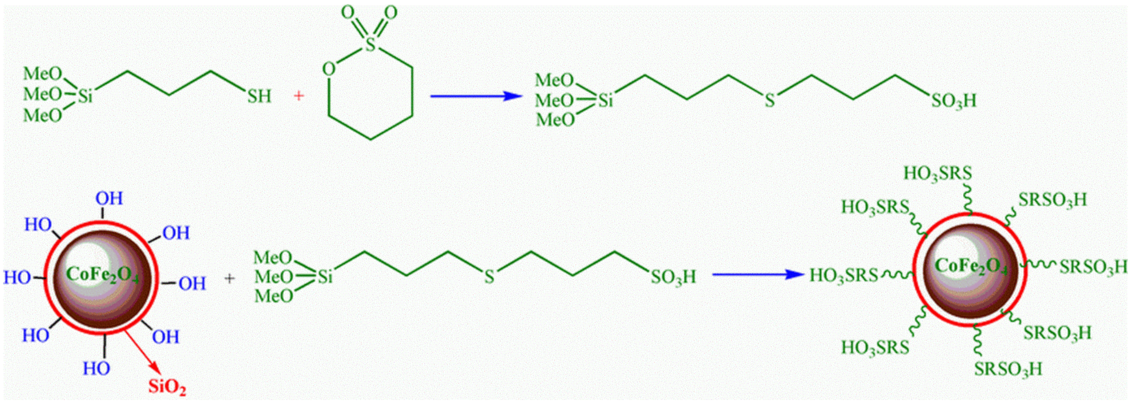
2. Experimental

2.1. General

All the chemicals were of analytical grade and used without further purification. FT-IR spectra were obtained using BOMEM MBSeries 1998 FT-IR spectrometer. NMR spectra were recorded in $CDCl_3$ on a Bruker Avance DPX 400 MHz spectrometer.

2.2. Synthesis of sulfonic acid supported on silica-coated cobalt ferrite Cobalt ferrite

MNPs were prepared using the method reported by Maaz et al [6]. Coating of $CoFe_2O_4$ nanoparticles with a layer of silica was achieved through Stober method [7-9]. A one-pot procedure was used to synthesize sulfonic acid supported on $CoFe_2O_4@SiO_2$ as follows [10]. At first, a mixture of 3-meraptopropyl trimethoxysilane (5.9 ml, 32 mmol) and 1,3-propanesultone (3.25 ml, 32 mmol) was heated at 110 °C for 24 h with continuous stirring under N_2 atmosphere. The product of this step was dissolved in 25 mL of toluene followed by addition of $CoFe_2O_4@SiO_2$ (1.1 g) and the mixture was refluxed for 24 h. Finally, the produced sulfonic acid silica-coated MNPs ($CoFe_2O_4@SiO_2$-RSR-SO_3H) were magnetically separated and washed twice with toluene and ether. A schematic representation of $CoFe_2O_4@SiO_2$-RSR-SO_3H synthesis is shown in Scheme 2.



Scheme 2. Schematic representation of the formation of HSO_3-RSR-SiMNPs catalyst

2.3. General procedure of catalytic 1-aminoalkyl-2-naphthol synthesis

To a mixture of an aldehyde (1 mmol), acetamide (1 mmol), 2-naphthol (1.2 mmol) and 0.05 g $CoFe_2O_4@SiO_2$- RSR-SO_3H catalyst was added and the mixture was stirred for an appropriate time at 80 °C. After completion of the reaction (monitored by TLC), CH_3Cl was added to dilute the reaction mixture and the organic layer was simply decanted by means of an external magnet. The isolated solution was purified on a silica-gel plate to obtain pure product. The products were identified by FT-IR and ^1H NMR matches with the literature.

3. Result and discussion

At the outset, the three-component reaction of benzaldehyde, acetamide and 2-naphthol was investigated in various conditions at 80 ° C. Initially, we have focused our attention on the effect of the solvent on model reaction; we have studied the effect of different solvents such as CH_3CN, THF, CH_2Cl_2, Toluene and EtOH in the presence of HSO_3-RSR-SiMNPs as catalyst. But solvent -free approach showed better results (see Table 1). Secondly, to investigate the effect of SO_3H moiety on this catalysis reaction, we have also examined SiMNPs in similar reaction in the separate experiment. As seen in Table 1, SiMNPs showed the weak catalytic activity for the 1-aminoalkyl-2-naphthol synthesis.

Table 1. Effect of various catalysts and solvents on the synthesis 1-aminoalkyl-2-naphthol synthesis

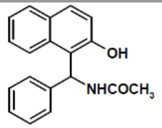
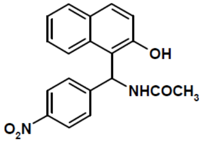
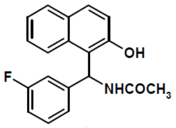
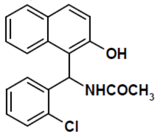
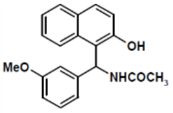
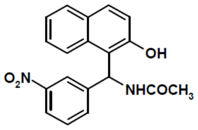
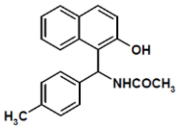
Entry	Catalyst	Solvent	Time (min)	Yield[b](%)
1	HSO_3-RSR-SiMNPs	CH_3CN	25	88
2	HSO3-RSR-SiMNPs	THF	40	60
3	HSO_3-RSR-SiMNPs	CH_2Cl_2,	40	86
4	HSO3-RSR-SiMNPs	Toluene	45	55
5	HSO_3-RSR-SiMNPs	EtOH	40	75
7	SiMNPs	Neat	100	35

[a] All reaction conditions: benzaldehyde (1 mmol), acetamide (1 mmol), 2-naphthol (1.2 mmol), Catalyst (0.05 g) at 80 °C

[b] Isolated yield

Then, this condensation reaction with various aldehyde, acetamide and 2-naphthol, in the presence of HSO_3-RSR-SiMNPs as the catalyst was explored under the optimized reaction conditions described above, and the results are presented in Table 2.

Table 2. Synthesis of diversified 1-aminoalkyl-2-naphthol synthesis in the presence of HSO_3-RSR-SiMNPs [a]

Entry	Aldehyde	Product	Time (min)	Yield[b] (%)
1	R=H		10	96
2	R= 4-NO_2		20	86
3	R=3 F		15	88
4	R= 2-Cl		15	88
5	R= 3-OMe		15	93
6	R= 3-NO_2		20	84
7	R= 4-CH_3		15	90

[a] All reaction condition: aldehydes (1 mmol), acetamide (1 mmol) and 2-naphthol (1.2 mmol), Catalyst (0.05 g) at 80 ^{o}C

[b] Isolated yields

It can easily be seen that this one-pot, three component condensation completed within 10–20 min and the products were isolated in good to excellent yields.

The nanocatalyst reusability was also investigated. For this purpose, the same model reaction was again studied under the optimized conditions. After the completion of the first reaction, the product was diluted with CH_3Cl and the solution was removed by magnetic decantation.

The left used catalyst was washed with methanol and $CHCl_3$ and dried at 60 °C for 30 min prior to the next run. A new reaction was then conducted with fresh reactants under the same reaction conditions. We could successfully use this catalyst in ten successive reactions with no significant loss of catalytic activity (see Table 3).

Table. 3. Catalyst recycling experiments for 1-aminoalkyl-2-naphthol synthesis

Cycle	1 st	2 st	3 st	4 st	5 st	6 st	7 st	8 st	9 st	10 st
Yield(%)	95	94	94	93	93	91	91	89	88	88

[a] All reaction condition: benzaldehyde (1 mmol), amine (1 mmol1 mmol) and 2-naphthol (1.2 mmol), Catalyst (0.05g) at 80 ^{o}C, [b] Isolated yields

4. Conclusion

The immobilized sulfonic acid was shown to be an environmentally safe heterogeneous solid acid catalyst for synthesis of 1-aminoalkyl-2-naphthol derivatives under solvent-free conditions at 80 ^{o}C. This method offers several advantages including short reaction time, good to excellent product yields, simple workup, ease of separation of the magnetic catalyst, as well as the ability to tolerate a wide variety of substitutions in the reagents. Moreover, catalyst could be recovered from the reaction mixture by compartmentation with the aid of an external magnet and could be reused seven times with no significant loss of catalytic activity.

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