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Sulfonic acid-functionalized silica: A remarkably efficient heterogeneous reusable catalyst for the one-pot multi-component synthesis of amidoalkyl naphthols

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Abstract

A novel, efficient and one-pot method for preparation of amidoalkyl naphthol derivatives is reported using sulfonic acid-functionalized silica as an effective heterogeneous catalyst under thermal solvent-free conditions. This method has the advantages of high yields, a cleaner reaction, simple methodology, easy work-up and greener conditions. The catalyst is easily prepared, stable (up to 300 °C, reusable and efficient under the reaction conditions.

Keywords: Amidoalkyl naphthols; Multicomponent synthesis; Solid acid; Sulfonic acid-functionalized silica; Heterogeneous recyclable catalyst

1. Introduction

Multi-component reactions (MCRs) are a promising and vital field of chemistry because the synthesis of complicated molecules can be achieved in a very fast, efficient, and timesaving manner without the isolation of any intermediate. As a result, it requires minimum effort, which minimizes the environmental loading and is acceptable from a 'Green Chemistry' point of view. In recent years, the discovery of novel MCRs has become an increasingly active area of research, yielding novel chemical scaffolds for drug discovery. Thus, the development of new multi-component reactions is a popular area of research in current organic chemistry (Menendez 2006).

The preparation of amidoalkyl naphthols can be carried out by multi-component condensation of aryl aldehydes, 2-naphthol, and acetonitrile or amide in the presence of Lewis or Bronsted acid catalysts such as montmorillonite K10 clay (Kantevari 2007), $Ce(SO_4)_2$ (Selvam 2006), iodine (Das 2007), $K_5CoW_{12}O_{40}.3H_2O$ (Nagarapu 2007), sulfamic acid (Patil 2007), and cation-exchanged resins (Patil 2007). However, some of these catalysts suffer from the drawback of green chemistry such as prolonged reaction times, toxic reagents, expensive or highly acidic catalysts and low yields. The recovery and reusability of the catalyst is also a problem. Therefore, the development of a *catalytic* synthetic method for amidoalkyl naphthols still remains an active research area.

One of the most important objectives now is to adapt classical processes so that pollution effects are kept to a minimum, with both a reduction in energy and consumption of raw materials. Solid acid catalysts play a prominent role in organic synthesis under heterogeneous conditions (Modarresi-Alam 2007; Modarresi-Alam 2008; Mohammadi 2010; Nasrollahzadeh 2009; Sajadi 2011). In general, solid acid catalysts are mainly based on clay (Bahulayan 2002) and silica (Das 2007; Habibi 2010; Habibi 2011; Modarresi-Alam 2007; Nasrollahzadeh 2009). In terms of convenience, silica-based catalysts are inexpensive, easy to prepare, and insoluble in most of the organic solvents, which means they have the advantage of recovery and recycle from various reactions. Among various heterogeneous catalysts, several types of sulfonic acid-functionalized silica have been synthesized and applied as alternatives to traditional sulfonic resins in catalyzing chemical transformations (Mbaraka 2003; Diaz 2000; Wilson 2002). Sulfonic acid-functionalized silica behaves as an organic-inorganic hybrid (interphase) catalyst wherein a Bronsted acid

site has been selectively created. Recently, silica functionalized sulfonic acid as heterogeneous solid acid catalyst has been used to catalyze a variety of reactions (Karimi 2005; Das 2006; Shylesh 2004). The catalyst was prepared (Karimi 2005) by the immobilization of propyl thiol on silica using 3-mercaptopropyltrimethoxysilane followed by the selective oxidation of the thiol groups by aqueous H_2O_2 to the sulfonic-acid groups (Scheme 1). The catalyst shows high thermal stability (up to 300 °C) (Karimi 2005).

In continuation of our researches on the heterocycles (Nasrollahzadeh 2011; Sajadi 2011), we wish to describe a new, simple, mild and effective procedure for the one-pot synthesis of amidoalkyl naphthols via a multi-component reaction in the presence of sulfonic acid-functionalized silica as a recyclable catalyst (Scheme 1).

2. Experimental

2.1. General

All reagents were purchased from Merck and Aldrich and used without further purification. ^{13}C NMR and ^{1}H NMR spectra were recorded on Brucker, 300 and 500 MHz using TMS as an internal standard. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. IR spectra were recorded on a Shimadzu 470 spectrophotometer. TLC was performed on Merck-precoated silica gel 60-F254 plates.

2.2. General Procedure for the synthesis of amidoalkyl naphthols

A mixture of 2-naphthol (1 mmol), aldehydes (1 mmol), and urea or acetamide (1.2 mmol) and sulfonic acid-functionalized silica (0.09 g) was heated at 120 °C with stirring for 50 min. After completion of the reaction as indicated by TLC, the mixture was cooled to 25 °C, boiling EtOH was added and the mixture stirred for 5 min. The catalyst was recovered. Then solution was cooled to room temperature, the solid so obtained was filtered and recrystallized from aqueous EtOH (15%).The desired pure product(s) were characterized by comparison of their physical data with those Then, the cure of known compounds.

3. Result and Discussion

In the first set of experiments, we optimized the amount of sulfonic acid-functionalized silica as catalyst in the reaction between 2-naphthol, benzaldehyde and acetamide. The amount of sulfonic acid-functionalized silica was chosen to be 0.09 g. Thus, we continued preparation of amidoalkyl naphthols in an optimum model experiment: aldehyde (1 mmol), 2-naphthol (1 mmol), acetamide or urea (1.2 mmol) in the presence of sulfonic acid-functionalized silica (0.09 g) at 120 °C (Scheme 2, Table 1). As shown in Table 1, benzaldehyde and aromatic aldehhydes containing electron-withdrawing groups (such as nitro, halide group) or electron-donating groups (such as alkoxyl group) were employed and gave the corresponding amidoalkyl naphthols without the formation of any side products, in high to excellent yields and in short reaction times under thermal solvent-free conditions (Table 1, entry 1-14). Sulfonic acid-functionalized silica works under heterogeneous conditions but its reaction centres are highly mobile, as in a homogeneous catalyst. It is an inexpensive and non-hazardous solid acid catalyst. It can easily be handled and removed from the reaction mixture by simple filtration. The recovered catalyst was reused consecutive five times with a minimum variation of the yields of the products. This reusability demonstrates the high stability and turnover of solid silica-based sulfonic acid under operating condition. The simplicity, together with the use of inexpensive, non-toxic and environmentally benign catalyst under solvent free condition are other remarkable features of the procedure. All the products obtained were fully characterized by spectroscopic methods such as IR, ^{1}H NMR, ^{13}C NMR and also by comparison of the spectral data with those reported.

4. Conclusion

In conclusion, we have developed a novel and highly efficient method for the synthesis of amidoalkyl naphthols using silica solid sulfonic acid as a heterogeneous catalyst. The significant advantages of this methodology are high yields, simple work-up procedure, cleaner reaction and easy preparation and handling of the catalyst. The catalyst can be recovered by simple filtration and reused without loss of activity.

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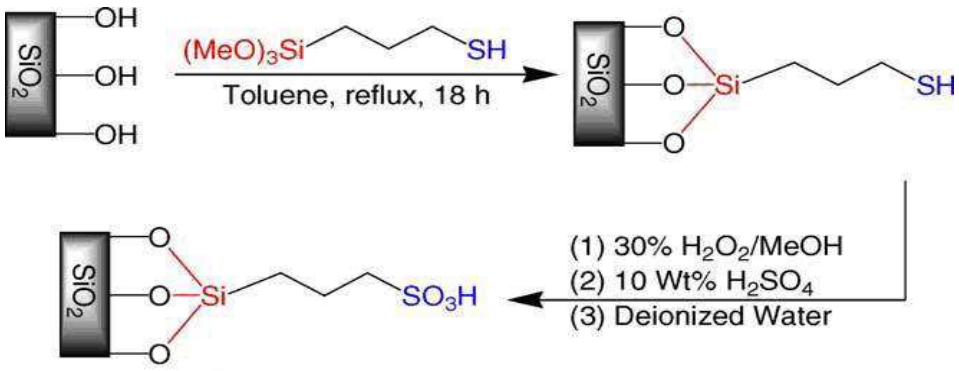
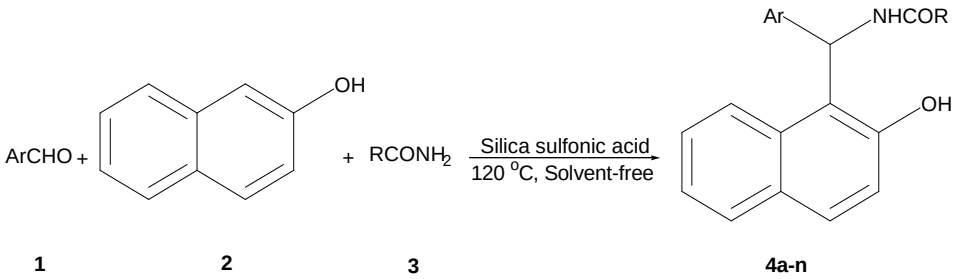


Scheme 1. Preparation of solid silica-based sulfonic acid



Scheme 2.

Table 1 Preparation of amidoalkyl naphthols catalyzed by sulfonic acid-functionalized silica under thermal and solvent-free conditions

Entry	Ar	R	Product	Yield[a] %	Mp (lit. mp) (reference)
1	C_6H_5	CH_3	**4a**	92	244-246 (241-243) (Selvam 2006)
2	2-ClC_6H_4	CH_3	**4b**	91	195-197 (194-196) (Patil 2007)
3	3-FC_6H_4	CH_3	**4c**	88	248-250 (248-249) (Patil 2007)
4	3-$OMeC_6H_4$	CH_3	**4d**	90	204-205 (203-205) (Kantevari 2007)
5	4-FC_6H_4	CH_3	**4e**	90	210-212 (209-210) (Selvam 2006)
6	4-ClC_6H_4	CH_3	**4f**	91	229-231 (224-227) (Selvam 2006)
7	4-BrC_6H_4	CH_3	**4g**	90	230-232 (228-230) (Patil 2007)
8	4-MeC_6H_4	CH_3	**4h**	89	221-223 (222-223) (Patil 2007)
9	4-$OMeC_6H_4$	CH_3	**4i**	87	184-186 (184-186) (Selvam 2006)
10	2,4-$Cl_2C_6H_3$	CH_3	**4j**	92	200-202 (198-199) (Selvam 2006)
11	C_6H_5	NH_2	**4k**	89	230-232 (230-232) (Patil 2007)
12	3-$OMeC_6H_4$	NH_2	**4l**	87	167-169 (166-168) (Kantevari 2007)
13	4-ClC_6H_4	NH_2	**4m**	92	168-170 (168-169) (Patil 2007)
14	4-BrC_6H_4	NH_2	**4n**	86	172-174 (170-172) (Patil 2007)

[a]Yields refer to the pure isolated products.