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Silica-bonded *S*-sulfonic acid a recyclable catalyst for the synthesis of coumarins

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Abstract

Silica-bonded *S*-sulfonic acid (SBSSA) was prepared by the reaction of 3-mercaptopropylsilica (MPS) and chlorosulfonic acid in chloroform. This solid acid has been employed as a recyclable catalyst for the synthesis of coumarins from phenols and β-keto-esters at 80 °C under solvent-free conditions.

Keywords: Silica-bonded *S*-sulfonic acid; Coumarins; Solvent-free; Phenols; β-Keto-esters

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The development of heterogeneous catalysts for fine chemical synthesis has become a major area of research. The potential advantages of these materials over homogeneous systems (simplified recovery and reusability; the potential for incorporation in continuous reactors and micro reactors) could lead to novel environmentally benign chemical procedures for use academia and industry [1]. Application of solid acids in organic transformations has an important role, because they have many advantages such as facile handling, decreased reactor and plant corrosion problems, and more environmentally safe disposal [2–5].

Coumarin derivatives are natural products widely distributed in the plant kingdom and their main applications are as fragrances, pharmaceuticals, and agrochemicals [6]. Synthesis of coumarins has been carried out by the Pechmann reaction [7], i.e. by condensation of phenols with β-keto-esters in acidic media. A large number of reagents have been used for this reaction, e.g. H_2SO_4 [7], $HClO_4$ [8], P_2O_5 [9] and chloroaluminate ionic liquid [10]. However, these reagents are required in excess and their corrosive nature makes them difficult to handle, and formation of several side products is a problem. Several other acid catalysts, including Lewis acids, are known to affect this condensation [11]. However, moisture sensitivity of the majority of Lewis acids to the water produced in the Pechmann reaction renders them unsuitable for use in large-scale applications. Other methods have utilized ionic liquids [10,12] and microwave irradiation [13], but these methods also generate strongly acidic by-products and/or they utilize highly expensive and nonrecyclable reagents. Recently, a number of heterogeneous catalysts such as Nafion-H [14], zeolite H-BETA, Amberlyst 15 [15], montmorillonite clay [16], silica sulfuric acid [17], alum [18], water-tolerant sulfonic acid nanoreactor [4], scandium (III) triflate [19], and ultrasound irradiation [20] have been employed in the Pechmann condensation.

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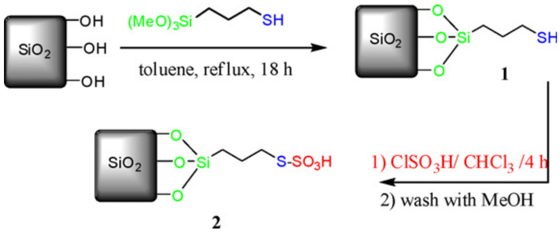
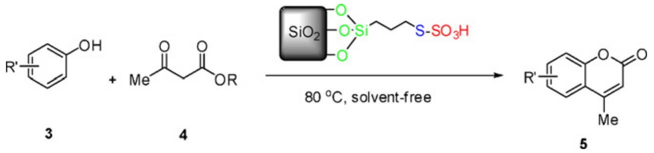


Scheme 1. Preparation of silica-bonded *S*-sulfonic acid (SBSSA).

Table 1
Pechmann reaction of resorcinol with ethyl acetoacetate employing different sulfonic acids.

Entry	Acid	Reaction conditions	The amounts of catalyst (mol%)	Time (min)	Yield (%)[a]
1	H_2SO_4	Room temperature	1 mL	12–24 h	82–90 [7c]
2	*p*-TsOH	130 °C	0.7	60	65 [4]
3	SBA-15	130 °C	430 mg	60	NR [4]
4	Silica gel	130 °C	430 mg	60	NR [4]
5	Nanoreactor	130 °C	0.7	60	90 [4]
6	Silica sulfuric acid	80 °C	15.6	30	93 [17]
7	Alum	65 °C	20	150	91 [18]
8	SBSSA	80 °C	3.4	15	89

[a] Isolated yield.



Scheme 2. Silica-bonded *S*-sulfonic acid catalyzed condensation of phenols with ethyl or methyl acetoacetates.

Recently, we prepared silica-bonded *S*-sulfonic acid (SBSSA) **2** and used as a catalyst for the preparation of acylals [21] and quinoxalines [22] (Scheme 1).

Herein, we use SBSSA as a catalyst for the synthesis of coumarins. The catalytic activity of SBSSA, and some of the other reported acids was tested in the coupling reaction of resorcinol (1,3-dihydroxyphenol) with ethyl acetoacetate under solvent-free conditions (Table 1). The best results were obtained with 0.1 g (3.4 mol%) of SBSSA per 1 mmol of resorcinol at 80 °C. Encouraged by the above result, other coumarin derivatives were synthesized under the same conditions (Scheme 2).

Several types of phenolic substrates and β-keto-esters with different functionalities were used in the reaction. As could be seen in Table 2, the reaction was found to be employable a variety of substrates in general, yields were very

Table 2
SBSSA catalyzed condensation reaction of phenols with β-keto-esters to produce corresponding coumarin derivatives[a].

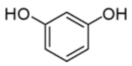
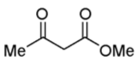
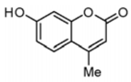
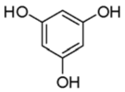
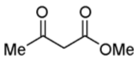
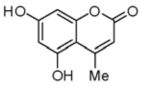
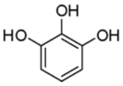
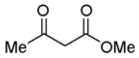
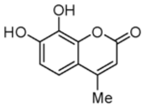
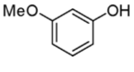
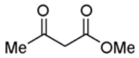
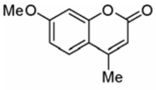
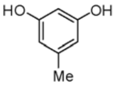
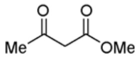
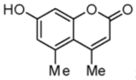
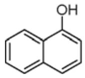
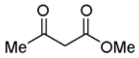
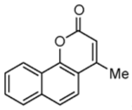
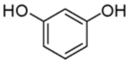
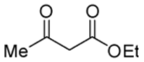
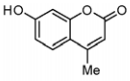
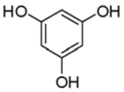
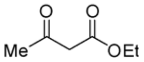
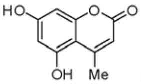
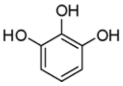
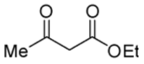
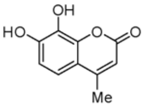
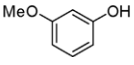
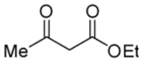
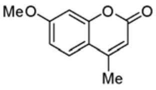
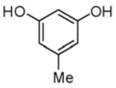
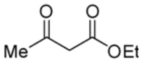
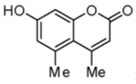
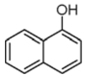
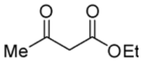
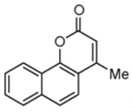
Entry	Phenol	β-Keto-ester	Product	Time (min)	Yield (%)[b]
1			 **5a**	15, 15, 15, 17, 17[c]	87, 85, 84, 86, 85[c]
2			 **5b**	15	86

Table 2 (*Continued*)

Entry	Phenol	β-Keto-ester	Product	Time (min)	Yield (%)[b]
3			 **5c**	15	89
4			 **5d**	12	90
5			 **5e**	10	84
6			 **5f**	15	84
7			 **5a**	15	89
8			 **5b**	15	84
9			 **5c**	15	85
10			 **5d**	15	85
11			 **5e**	10	86
12			 **5f**	15	86

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[a] The molar ratio of phenol (1 mmol), β-keto-ester (1.5 mmol), and SBSSA (0.1 g).

[b] Isolated yield.

[c] The SBSSA was used for four runs.

high. The experimental procedure is very simple and work up includes the addition of ethanol followed by filtration of the catalyst.

The possibility of recycling the catalyst was examined using the reaction of resorcinol (1 mmol) with methyl acetoacetate (1.5 mmol) in the presence of SBSSA (0.1 g) at 80 °C under solvent-free conditions. Upon completion, the reaction mixture was filtered and the remaining solid was washed with ethanol and the catalyst reused in the next reaction. The recycled catalyst could be reused four times without any additional treatment. No observation of any appreciable loss in the catalytic activity of SBSSA was observed (Table 2, entry 1).

In conclusion, SBSSA has been employed for the synthesis of coumarins by the reaction of phenolic derivatives with β-keto-esters. The attractive features of this procedure are the mild reaction conditions, high conversions, clean reaction profiles, reusable and environmentally friendly catalyst.

1. Catalyst characterization

Sulfur content of the samples by conventional elemental analysis was 16.12%. The SBSSA was placed in an aqueous NaCl solution, the solution pH dropped virtually instantaneously to pH ≈ 1.85, as ion exchange occurred between protons and sodium ions (proton exchange capacity: 0.34 mmol/g of SBSSA [21,22].

2. General procedure, synthesis of coumarines 5

To a mixture of phenolic substrate **3** (1 mmol) and β-keto-ester (1.5 mmol), SBSSA (0.1 g) was added and magnetically stirred at 80 °C. The progress of the reaction was followed by TLC. After completion of the reaction, warm ethanol (10 mL) was added and filtered, and the remaining was washed with warm ethanol (2× 10 mL) in order to separate catalyst. Ethanol was evaporated under reduced pressure and crude product was recrystallized from EtOH.

3. ^{1}H and ^{13}C NMR data of compounds

Compound **5a**: mp 186–188 °C (Lit. [17] mp 187–188 °C); ^{1}H NMR (500 MHz, $CDCl_3$-DMSO-d_6, δ ppm): 2.29 (s, 3H), 5.96 (s, 1H), 6.71–6.74 (m, 2H), 7.34 (d, 1H, $J = 8.4$ Hz), 9.74 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$-DMSO-d_6, δ ppm): 19.00, 103.44, 111.20, 112.93, 113.54, 126.03, 153.41, 155.61, 161.65, and 162.02.

Compound **5b**: mp 284–286 °C (Lit. [17] mp 285–287 °C); ^{1}H NMR (500 MHz, $CDCl_3$-DMSO-d_6, δ ppm): 2.44 (s, 3H), 5.67 (d, 1H, $J = 1.1$ Hz), 6.17 (d, 1H, $J = 2.3$ Hz), 6.19 (d, 1H, $J = 2.3$ Hz), 9.48 (s, 1H), 9.59 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$-DMSO-d_6, δ ppm): 24.32, 95.64, 99.97, 103.37, 109.53, 156.14, 157.13, 158.29, 161.42, and 162.17.

Compound **5c**: mp 242–244 °C (Lit. [11c] mp 241–243 °C); ^{1}H NMR (500 MHz, $CDCl_3$-DMSO-d_6, δ ppm): 2.20 (s, 3H), 5.88 (s, 1H), 6.67 (d, 1H, $J = 8.6$ Hz), 6.84 (d, 1H, $J = 8.6$ Hz), 8.63 (brs, 2H). ^{13}C NMR (125 MHz, $CDCl_3$-DMSO-d_6, δ ppm): 19.12, 111.10, 112.60, 113.59, 115.68, 132.36, 143.55, 149.35, 153.96, and 161.35.

Compound **5d**: mp 156–158 °C (Lit. [19] mp 155–157 °C); ^{1}H NMR (500 MHz, $CDCl_3$-DMSO-d_6, δ ppm): 2.44 (s, 3H), 3.91 (s, 3H), 6.18 (s, 1H), 6.86 (d, 1H, $J = 2.5$ Hz), 6.90 (dd, 1H, $J_1 = 8.8$ Hz, $J_2 = 2.5$ Hz), 7.54 (d, 1H, $J = 8.8$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$-DMSO-d_6, δ ppm): 19.08, 56.16, 101.29, 112.41, 112.71, 114.02, 125.93, 152.93, 155.76, 161.69, and 163.09.

Compound **5e**: mp 256–258 °C (Lit. [19] mp 256–257 °C); ^{1}H NMR (500 MHz, $CDCl_3$-DMSO-d_6, δ ppm): 2.08 (s, 3H), 2.38 (s, 3H), 5.72 (s, 1H), 6.34 (s, 2H), 9.56 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$-DMSO-d_6, δ ppm): 21.81, 24.29, 107.38, 108.48, 112.32, 112.41, 143.05, 155.44, 155.50, 156.81, and 161.44.

Compound **5f**: mp 166–168 °C (Lit. [17] mp 166–169 °C); ^{1}H NMR (500 MHz, $CDCl_3$-DMSO-d_6, δ ppm): 2.55 (s, 3H), 6.40 (s, 1H), 7.62 (d, 1H, $J = 8.7$ Hz), 7.65–7.68 (m, 2H), 7.72 (d, 1H, $J = 8.7$ Hz), 7.89–7.91 (m, 1H), 8.58–8.60 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$-DMSO-d_6, δ ppm): 19.70, 114.79, 115.62, 120.75, 123.08, 123.58, 124.56, 127.56, 128.07, 129.02, 135.20, 151.02, 153.83, and 161.32.

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