Res Chem Intermed
DOI 10.1007/s11164-014-1578-9

Sulfonic acid-functionalized mesoporous silica nanoparticles (SAMSNs): a recoverable heterogeneous acid catalyst for green synthesis of dicoumarols

Ebrahim Mehrasbi · Yaghoub Sarrafi · Amir Vahid · Heshmatollah Alinezhad

Received: 24 October 2013 / Accepted: 25 February 2014

Abstract Sulfonic acid-functionalized mesoporous silica nanoparticles (SAMSNs) have been used as a highly efficient and recoverable heterogeneous acid catalyst for green synthesis of dicoumarols by reaction of different aldehydes with 4-hydroxycoumarin in aqueous media. High to excellent yields were obtained. This mesoporous catalyst is readily recovered and can be reused at least six times without significant loss of its catalytic activity.

Keywords Green synthesis · Dicoumarols · 4-Hydroxycoumarin · Sulfonic acid-functionalized mesoporous silica · Aqueous medium

Introduction

Coumarins constitute a prominent class of organic compounds utilized in the cosmetics, food, pharmaceutical, and agrochemical industries [1–3]. Among the coumarin derivatives, dicoumarols have attracted much attention because of their biological importance and wide-ranging pharmacological activity, for example anticoagulant, antitumor, antihelminthic, insecticidal, hypnotic, antifungal, and HIV protease inhibitory activity [3–12]. Dicoumarol, 3,3′-methylenebis(4-hydroxycoumarin), a naturally occurring anticoagulant drug that functions as a vitamin K antagonist, was first isolated from sweet clover (*Melilotus alba* and *Melilotus officinalis*) [13, 14]. Neodymium(III) and lanthanum(III) complexes of dicoumarol have substantial cytotoxic activity [15]. Notably, clinical trials have revealed that

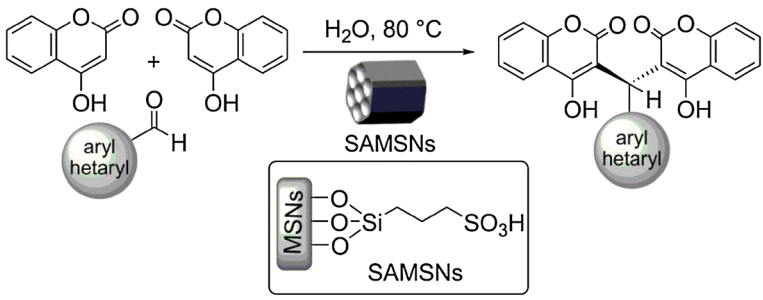
E. Mehrasbi · Y. Sarrafi (✉) · A. Vahid · H. Alinezhad
Department of Organic Chemistry, Faculty of Chemistry, University of Mazandaran, 47416 Babolsar, Iran
e-mail: ysarrafi@umz.ac.ir

Published online: 14 March 2014

dicoumarols are active against prostate cancer, malignant melanoma, and metastatic renal cell carcinoma [16–18].

Synthesis of dicoumarols is usually achieved by condensation of 4-hydroxycoumarin with aldehydes. Attempts to synthesize of dicoumarols over such catalysts as molecular iodine [19], Et_2AlCl_3 [20], DBU [21], $MnCl_2$ [22], $POCl_3$ in dry DMF [23], SO_3H-functionalized ionic liquids [24], [bmim][BF_4] [25], tetrabutylammonium bromide (TBAB) [26], phosphotungstic acid [27], Zn(proline)$_2$ [28], and sulfated titania [29] have been reported. Catalyst-free condensation reactions under thermal and microwave irradiation have also been developed [30]. Although each of these methods has merit, some have such disadvantages as long reaction time, expensive reagents, harsh conditions, low product yields, and use of environmentally harmful toxic catalysts. Moreover, the main disadvantage of almost all methods is that the catalysts are damaged in the workup procedure and cannot be recovered. Therefore, to avoid these limitations there is still a need for development of a better process for synthesis of dicoumarol derivatives in terms of operational simplicity, reusability of the catalyst, and economic viability.

Heterogeneous acid catalysts have attracted much attention in organic synthesis because of numerous advantages which include reusability, environmental compatibility, non-corrosiveness, and ease of separation, compared with their hazardous and corrosive homogeneous counterparts [31–37]. Among the different solid acid catalysts, mesoporous silica grafted with sulfonic acid has attracted extensive interest because of its unique properties, including high surface area, large pore volume, uniform hexagonal array, tunable pore diameter, and excellent thermal stability [38–41]. Incorporation of sulfonic acid groups on porous silica supports produces highly convenient solid acid catalysts with the advantages of homogeneous catalysts [42]. For these reasons, development of acid-functionalized mesoporous silica as recoverable heterogeneous acid catalysts for the synthesis of heterocyclic compound is a topic of current interest. In continuation of our ongoing effort to develop new and eco-friendly synthetic methods [43–46], we report herein a novel, environmentally benign, facile, and efficient method for synthesis of dicoumarols using sulfonic acid-functionalized mesoporous silica nanoparticles (SAMSNs) as a green and recoverable solid acid catalyst (Scheme 1).



Scheme 1 Synthesis of dicoumarol derivatives catalyzed by SAMSNs

Experimental

General

All chemicals were purchased from Merck, Fluka, and Sigma–Aldrich. Reactions were monitored by thin-layer chromatography (TLC). X-ray diffraction (XRD) patterns were recorded on a Seifert TT 3000 diffractometer using Cu Kα radiation of wavelength 0.15405 nm. Diffraction data were recorded in the region $2\theta = 1$–$10°$ at intervals of $2\theta = 0.01°$. A scanning rate of 1.0°/min was used. Scanning electron micrographs were recorded using a Zeiss (Oberkochen, Germany) DSM 962. Samples were deposited on a sample holder with adhesive carbon foil and sputtered with gold. Physisorption of nitrogen was measured at 77 K by use of a Belsorp-mini porosimeter. Pore-size distribution was calculated from the desorption branch by use of the Barrett–Joyner–Halenda (BJH) method [47]. Melting points were measured on an electrothermal 9100 apparatus. NMR spectra were recorded with a Bruker DRX-400 Avance instrument (400.1 MHz for ^{1}H and 100.6 MHz for ^{13}C). IR spectra were recorded on an FT-IR Bruker vector 22 spectrometer. Elemental analysis was performed with a Heraeus CHN-O Rapid analyzer.

Preparation of sulfonic acid-functionalized mesoporous silica nanoparticles (SAMSNs)

Well-ordered mesoporous silica nanoparticles (MSNs) were synthesized by a method described elsewhere [46]. Typically, 3.0 g MSNs was evacuated at 150 °C then excess 3-mercaptopropyltrimethoxysilane (MPTS) in dry toluene was added. The mixture was heated under reflux for 6 h and the solid was isolated by filtration, washed with dry toluene, and dried in air. The –SH groups were converted into $–SO_3H$ groups by mild oxidation with H_2O_2 (stirring for 24 h at 60 °C with excess oxidant). The solid was isolated by filtration, washed with water and ethanol, acidified with 0.1 M H_2SO_4, and thoroughly washed with water to remove all traces of liquid acid. The solid material was finally dried at 60 °C overnight. The amount of sulfonic acid groups of the SAMSNs, which was determined by acid–base titration, was found to be 0.83 mmol g^{-1}.

General procedure for synthesis of dicoumarols

Mixtures of 4-hydroxycoumarin (2 mmol), aldehyde (1 mmol), SAMSNs (0.025 g), and water (3 mL) were stirred at 80 °C for different times (Table 5). After completion of the reactions (as monitored by TLC), the mixtures were cooled to room temperature. The crude products were extracted with dichloromethane and concentrated to furnish the product.

Physical and spectral data of selected products

3,3′-((4-Nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) [19]

Yellow powder, mp 233–235 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 6.14 (1H, s, CH), 7.43 (6H, m, ArH), 7.69 (2H, t, $J = 7.6$ Hz, ArH), 8.01 (1H, d, $J = 7.6$ Hz,

ArH), 8.10 (1H, d, $J = 7.6$ Hz, ArH), 8.20 (2H, d, $J = 9.2$ Hz, ArH), 11.39 (1H, s, OH), 11.59 (1H, s, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_c (ppm) 36.52, 103.27, 104.76, 116.23, 116.67, 116.75, 116.82, 123.89, 124.47, 124.51, 125.17, 125.24, 127.58, 133.39, 143.37, 146.87, 152.32, 152.57, 164.85, 166.45, 167.01, 169.12. Anal. Calcd. for $C_{25}H_{15}NO_8$: C, 65.65; H, 3.31; N, 3.06. Found: C, 65.75; H, 3.39; N, 3.11.

3,3′-(Naphthalen-2-ylmethylene)bis(4-hydroxy-2H-chromen-2-one) 3m [3]

Off-white powder, mp 265–267 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H (ppm) 6.50 (1H, s, CH), 7.34 (3H, m, ArH), 7.41 (4H, m, ArH), 7.62 (3H, m, ArH), 7.80 (3H, m, ArH), 7.91 (2H, d, $J = 8$ Hz, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): (ppm) 36.86, 104.59, 116.48, 118.47, 124.23, 124.41, 124.86, 125.67, 126.26, 126.56, 127.68, 128.01, 128.05, 132.04, 132.39, 133.52, 138.29, 152.76, 165.25, 165.88. Anal. Calcd. for $C_{29}H_{18}O_6$: C, 75.32; H, 3.92. Found: 75.41; H, 3.96.

3,3′-((2-Chloro-5-nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) ***3o***

Off-white powder, mp 277–279 °C; IR (KBr): 3,495 (OH), 3,076 (OH), 1,688 and 1,612 (CO), 1,525 and 1,345 (NO), 763 (C–Cl) cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H (ppm) 6.21 (1H, s, CH), 7.44 (4H, m, ArH), 7.41 (1H, d, $J = 8.8$ Hz, ArH), 7.68 (2H, m, ArH), 8.08 (2H, m, ArH), 8.14 (1H, m, ArH), 8.37 (1H, m, ArH), 11.02 (1H, s, OH), 11.77 (1H, s, OH). ^{13}C NMR (100 MHz, DMSO-d_6): (ppm) 35.94, 116.74, 123.43, 124.56, 124.69, 125.23, 131.66, 133.38, 135.94, 140.37, 146.61. Anal. Calcd. for $C_{25}H_{14}ClNO_8$: C, 61.05; H, 2.87; N, 2.85. Found: C, 61.11; H, 2.91; N, 2.88.

Results and discussion

First, the mesoporous silica nanoparticles (MSNs) were prepared in accordance with our previous work [46]. In the next step, the surface of the MSNs was functionalized by use of 3-mercaptopropyltriethoxysilane (MPTS). The thiol groups were then converted into sulfonic acid groups by mild oxidation with H_2O_2 (Fig. 1).

Sulfonated mesoporous silica nanoparticles were characterized by X-ray diffraction (XRD), N_2 adsorption/desorption, FT-IR spectroscopy, and scanning electron microscopy (SEM). Powder X-ray diffraction patterns of MSNs and SAMSNs are shown in Fig. 2.

For the MSNs five well-defined Bragg peaks at low angles are apparent; these can be indexed to the (1 0 0), (1 1 0), (2 0 0), (2 1 0), and (3 0 0) reflections corresponding to a hexagonal lattice (i.e. MCM-41). When the surface of mesoporous silica is functionalized with the propylsulfonic acid groups a decrease in the intensity of the peaks is observed, however the two-dimensional hexagonal array of mesoporous structure is retained. The specific surface area and total pore volume of the SAMSNs determined from N_2 adsorption–desorption isotherms were 366 m^{-2} g^{-1} and 0.36 cm^{-3} g^{-1}, respectively [47].

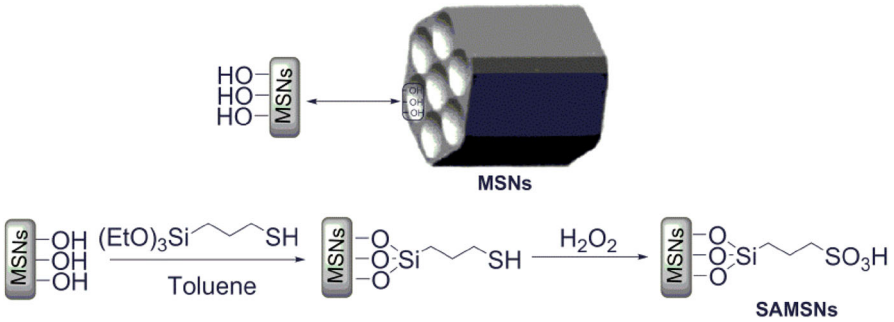


Fig. 1 Preparation of sulfonic acid-functionalized mesoporous silica nanoparticles (SAMSNs)

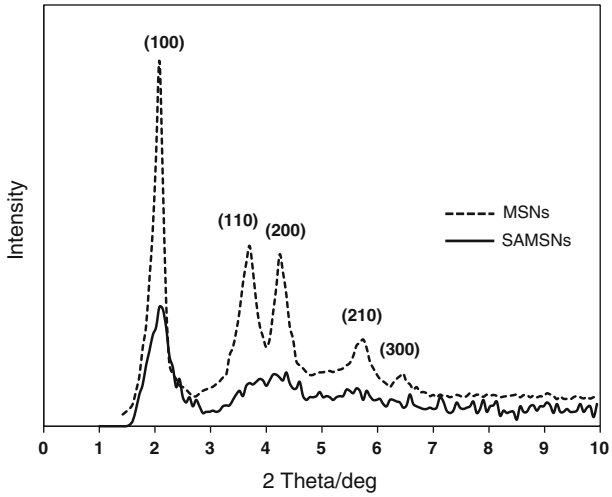


Fig. 2 XRD patterns of the calcined MSNs and SAMSNs

FT-IR spectra of MSNs and SAMSNs are shown in Fig. 3. Anchoring of propylsulfonic acid groups in the pore channels of the mesoporous materials is apparent from the methylene stretching bands in the 2,850–2,950 cm^{-1} region. Also, the SEM images (Fig. 4) showed that the sulfonic acid-functionalized MSNs were present as uniform particles with spherical morphology.

To study the catalytic activity of the prepared SAMSNs, we examined the reaction of 4-hydroxycoumarin with benzaldehyde, as simple model substrate, in aqueous media, using a wide variety of catalysts. As indicated in Table 1, the best results, in terms of yield and reaction time, was obtained by use of the SAMSNs catalyst (entry 10). The acid catalysts alum, sulfamic acid, PTSA, and Amberlist-15 gave moderate yields of the corresponding dicoumarols (entries 2–5). The K10–catalyzed reaction gave a much lower yield. The better catalytic activity of the SAMSNs may be because of their higher surface area, which enhanced chemical accessibility of the substrate to the anchored acid groups. When SiO_2 and ZnO nanoparticles were used, moderate

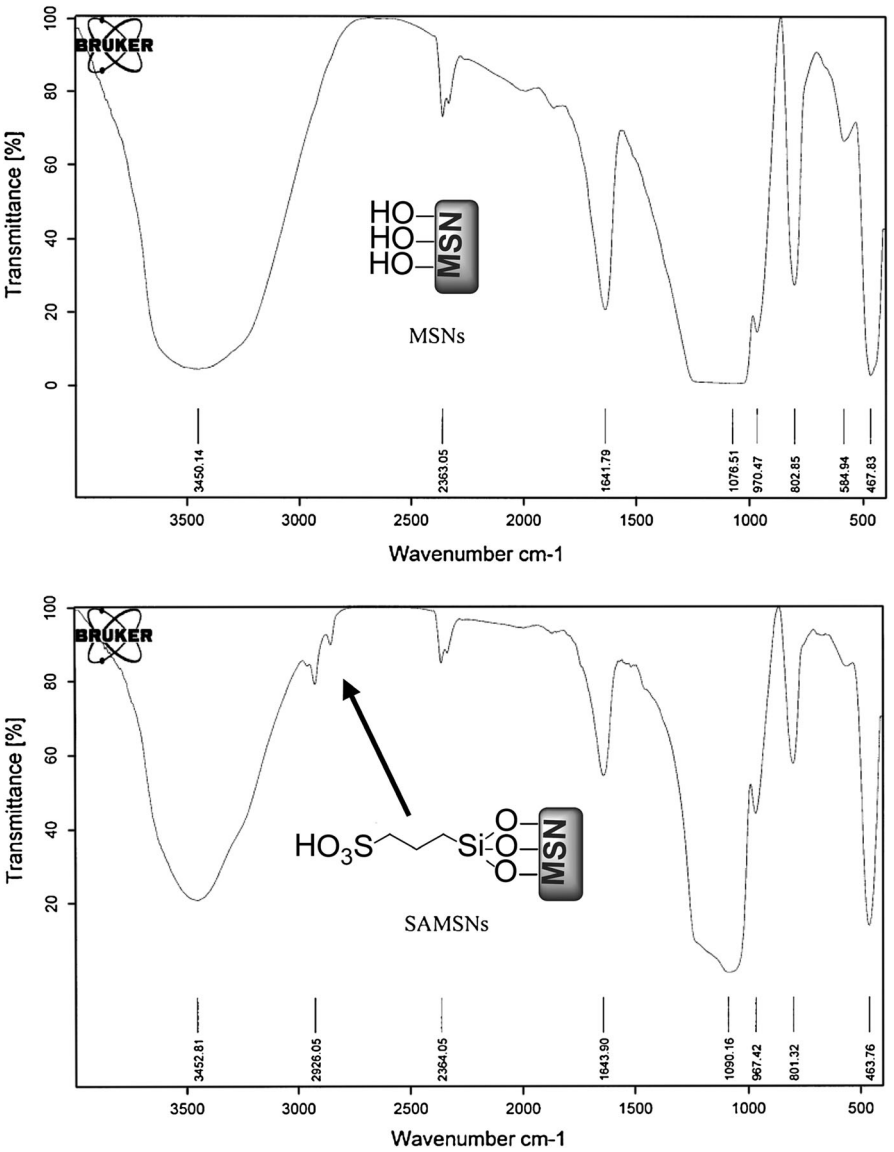


Fig. 3 IR spectra of MSNs and SAMSNs

yields of product were obtained after a longer reaction time (entries 7, 8). When the reaction was conducted with MSNs, longer reaction times were required and significantly lower yields were obtained. When the reaction was attempted without a catalyst, only a trace of product was formed (entry 1).

We next studied the effect of the amount of SAMSNs on the model reaction. As indicated in Table 2, the best results were obtained by use of 0.025 g SAMSNs; on further increasing the amount of SAMSNs the yield of the reaction was almost

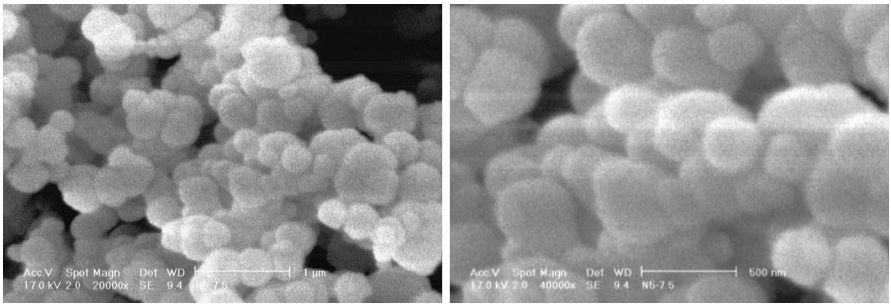
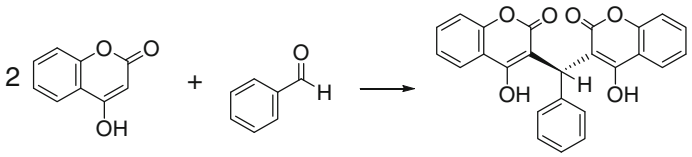


Fig. 4 SEM images of SAMSNs

Table 1 Optimization of the catalyst for the synthesis of dicoumarols in water



1a **2a** **3a**

Entry	Amount of catalyst[a] (0.05 g)	Time	Yield (%)[b]
1	–	24 h	Trace
2	Alum	120 min	65
3	Sulfamic acid	120 min	60
4	PTSA	120 min	50
5	Amberlist-15	120 min	57
6	Montmorillonite K10	5 h	33
7	Nano-SiO_2	5 h	55
8	Nano-ZnO	5 h	60
9	MSNs	5 h	42
10	SAMSNs	60 min	80

[a] Reaction conditions: benzaldehyde (1 mmol) and 4-hydroxycoumarin (2 mmol) in H_2O (3 mL) at room temperature

[b] Isolated yields

unaffected. The yield decreased when the amount of catalyst was reduced to 0.015 g (Table 2, entry 4), and prolonging the reaction time did not improve the yield (Table 2, entry 5).

During optimization of the reaction conditions, the effect of temperature on reaction rate and product yield was investigated (Table 3). When the reaction was conducted at temperatures ranging from room temperature to 100 °C, 80 °C was found to be the most suitable reaction temperature (Table 3, entry 3). The reaction proceeded sluggishly at lower temperatures and lower yields of the product were obtained (Table 3, entries 1

Table 2 Influence of the amount of SAMSNs in synthesis of dicoumarols[a]

Entry	SAMSNs (g)	Time (min)	Yield (%)[b]
1	0.1	60	82
2	0.05	60	80
3	0.025	60	80
4	0.015	120	67
5	0.015	240	70

[a] Reaction conditions: benzaldehyde (1 mmol) and 4-hydroxycoumarin (2 mmol) in H_2O (3 mL) at room temperature

[b] Isolated yields

Table 3 Effect of temperature on the SAMSNs-catalyzed synthesis of dicoumarols[a]

Entry	Temperature (°C)	Time (min)	Yield (%)[b]
1	RT	60	80
2	60	40	88
3	80	20	96
4	100	20	94

[a] Reaction conditions: benzaldehyde (1 mmol) and 4-hydroxycoumarin (2 mmol) in H_2O (3 mL) in the presence of 0.025 g SAMSNs

[b] Isolated yields

Table 4 Effect of solvent on the SAMSNs-catalyzed synthesis of dicoumarols

Entry	Solvent[a,b]	Time (min)	Yield (%)[c]
1	THF	20	80
2	DMSO	20	68
3	EtOH	20	88
4	MeOH	20	85
5	H_2O	20	96
6	Solvent-free	20	75

[a] Reaction conditions: benzaldehyde (1 mmol) and 4-hydroxycoumarin (2 mmol) in the presence of 0.025 g SAMSNs at 80 °C

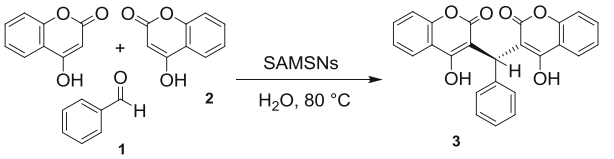
[b] Solvent: 3 mL

[c] Isolated yields

and 2). However, no increase in the rate of reaction was observed when the reaction temperature was increased from 80 to 100 °C (Table 3, entry 4).

To improve the yields further, the reaction was performed in different solvents and without solvent (Table 4). In polar protic solvents, for example MeOH and EtOH, relatively high yield of the product was obtained. However, when the reaction was performed in water, the product was obtained in excellent yield. The

Table 5 Synthesis of different dicoumarol derivatives **3** catalyzed by SAMSNs



1 2 3

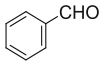
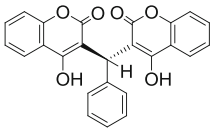
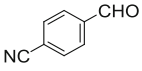
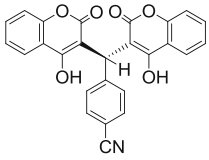
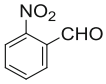
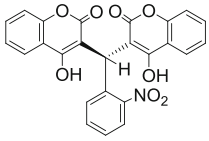
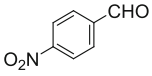
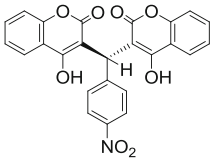
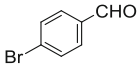
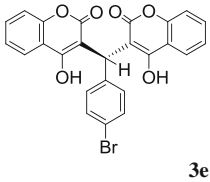
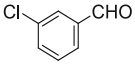
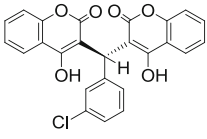
Entry	Aldehydes	Product[a]	Time (min)	Yield (%)[b,c]	[Ref.]
1		 **3a**	20	96	[19]
2		 **3b**	10	97	[29]
3		 **3c**	10	92	[30]
4		 **3d**	10	98	[19]
5		 **3e**	15	96	[29]
6		 **3f**	15	96	[30]

Table 5 continued

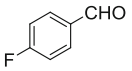
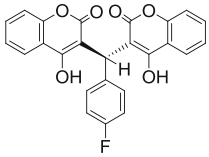
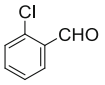
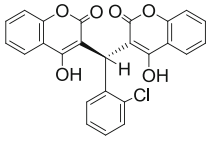
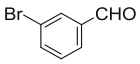
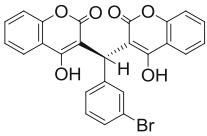
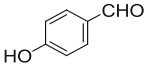
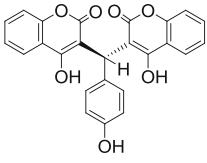
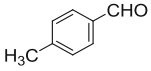
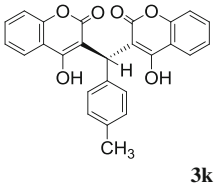
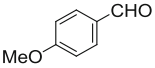
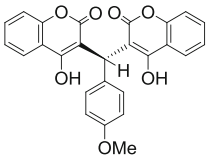
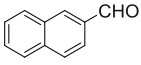
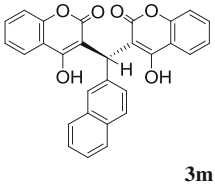
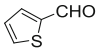
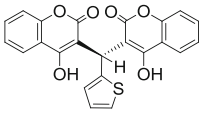
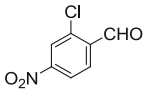
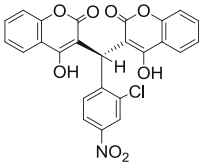
Entry	Aldehydes	Product[a]	Time (min)	Yield (%)[b,c]	[Ref.]
7		 **3g**	10	98	[26]
8		 **3h**	15	92	[30]
9		 **3i**	15	95	[29]
10		 **3j**	30	88	[19]
11		 **3k**	25	92	[29]
12		 **3l**	30	85	[19]
13		 **3m**	15	95	[3]

Table 5 continued

Entry	Aldehydes	Product[a]	Time (min)	Yield (%)[b,c]	[Ref.]
14		 **3n**	25	88	[19]
15		 **3o**	25	92	This work

[a] Reaction conditions: benzaldehyde (1 mmol) and 4-hydroxycoumarin (2 mmol) in the presence of 0.025 g SAMSNs in H_2O (3 mL) at 80 °C.
[b] Yields refer to pure isolated products.
[c] The products characterized by the comparison of their spectral (^{1}H NMR, ^{13}C NMR and IR) and physical data with those reported in the literature.

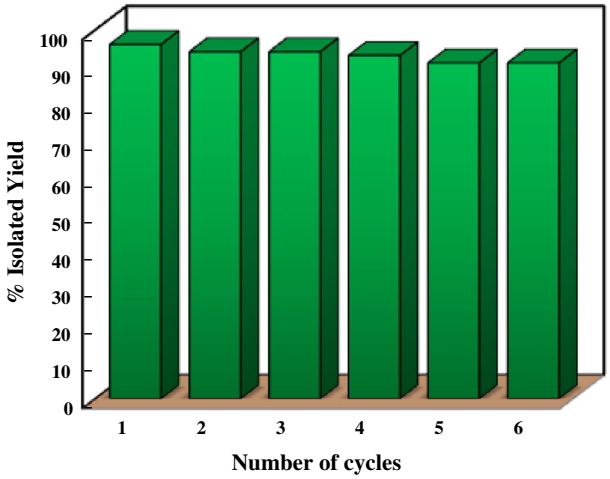


Fig. 5 Results from study of the reusability of the catalyst in the model reaction

hydrophobicity of the catalyst and organic starting materials in water might promote their interaction with each other and smooth conversion to the desired product.

In brief, the optimum reaction conditions for SAMSNs-catalyzed synthesis of dicoumarols were found to be benzaldehyde (1 mmol) and 4-hydroxycoumarin (2 mmol) in the presence of 0.025 g SAMSNs at 80 °C in aqueous media.

To assess the versatility of the method a series of aromatic aldehydes were studied under the optimum reaction conditions; the results are listed in Table 5. In all cases, the reactions gave the products in good to excellent yields in very short reaction times. Aromatic aldehydes with electron-withdrawing or electron-donating substituents, for example CN, NO_2, halogens, and CH_3, reacted smoothly under the optimized conditions affording the corresponding products (**3a**–**3i**, **3k** and **3m**) in high yields (Table 5), although lower yields of product were obtained from aromatic aldehydes with strongly electron-donating substituents, for example *p*-OCH_3 and *p*-OH. The acid-sensitive substrate thiophene-2-carbaldehyde gave the expected good yield.

Recovery and reuse of catalysts is a very important aspect of green chemistry. To investigate the recyclability of the catalyst, we conducted six successive cycles of the model reaction under the optimum reaction conditions using SAMSNs recycled from the previous run. The reaction proceeded smoothly even after six cycles, without any increase of reaction time or marked loss of yield (Fig. 5).

Conclusion

In summary, we have successfully developed a solid acid catalyst, sulfonic acid-functionalized mesoporous silica nanoparticles (SAMSNs), for synthesis of dicoumarol derivatives by reaction of aldehydes and 4-hydroxycoumarin in aqueous media. The SO_3H-functionalized catalyst was synthesized by incorporation of mercaptopropyl groups into mesoporous silica, then mild oxidation of SH to SO_3H. This catalyst can be recovered easily and reused over several reaction cycles without substantial loss of reactivity.

Acknowledgments The authors acknowledge the University of Mazandaran for financial support of this research.

References

1. J.W. Hinman, H. Hoeksema, E.L. Caron, W.G. Jackson, J. Am. Chem. Soc. **78**, 1072 (1956)
2. K.M. Khan, S. Iqbal, M.A. Lodhi, G.M. Maharvi, U. Zia, M.I. Choudhary, R. Atta ur, S. Perveen, Bioorg. Med. Chem. **12**, 1963 (2004)
3. I. Manolov, C. Maichle-Moessmer, I. Nicolova, N. Danchev, Arch. Pharm. **339**, 319 (2006)
4. R. Nagashima, R. Reilly, G. O'Levy, Clin. Pharm. Ther. **1**, 22 (1969)
5. R.A. O'Reilly, J.I. Ohms, C.H. Motley, J. Biol. Chem. **244**, 1303 (1969)
6. Z.H. Chohan, A.U. Shaikh, A. Rauf, C.T. Supuran, J. Enzym. Inhib. Med. Chem. **21**, 741 (2006)
7. B. Musicki, A.M. Periers, P. Laurin, D. Ferroud, Y. Benedetti, S. Lachaud, F. Chatreaux, J.L. Haesslein, A. Iltis, C. Pierre, J. Khider, N. Tessot, M. Airault, J. Demassey, C. Dupuis-Hamelin, P. Lassaigne, A. Bonnefoy, P. Vicat, M. Klich, Bioorg. Med. Chem. Lett. **10**, 1695 (2000)
8. M.E. Marshall, J.L. Mohler, K. Edmonds, B. Williams, K. Butler, M. Ryles, L. Weiss, D. Urban, A. Bueschen, M. Markiewicz, G. Cloud, J. Cancer Res. Clin. Oncol. **120**(Suppl), S39 (1994)
9. A. Maucher, E. Von Angerer, J. Cancer Res. Clin. Oncol. **120**, 502 (1994)
10. J.C. Jung, J.H. Lee, S. Oh, J.G. Lee, O.S. Park, Bioorg. Med. Chem. Lett. **14**, 5527 (2004)
11. H. Zhao, N. Neamati, H. Hong, A. Mazumder, S. Wang, S. Sunder, G.W.A. Milne, Y. Pommier, T.R. Burke Jr, J. Med. Chem. **40**, 242 (1997)
12. P.C.M. Mao, J.F. Mouscadet, H. Leh, C. Auclair, L.Y. Hsu, Chem. Pharm. Bull. **50**, 1634 (2002)
13. B.Y. Liu, T. Raeth, T. Beuerle, L. Beerhues, Plant Mol. Biol. **72**, 17 (2010)
14. H. Madari, D. Panda, L. Wilson, R.S. Jacobs, Cancer Res. **63**, 1214 (2003)

15. I. Kostova, I. Manolov, I. Nicolova, S. Konstantinov, M. Karaivanova, Eur. J. Med. Chem. **36**, 339 (2001)
16. R.D. Thornes, L. Daly, G. Lynch, B. Breslin, H. Browne, H.Y. Browne, T. Corrigan, P. Daly, G. Edwards, E. Gaffney, J. Henley, T. Healy, F. Keane, F. Lennon, N. McMurray, S. O'Loughlin, M. Shine, A. Tanner, Cancer Res. Clin. Oncol. **120**(Suppl), S32 (1994)
17. M.E. Marshall, K. Butler, A. Fried, Mol. Biother. **3**, 170 (1991)
18. J.L. Mohler, L.G. Gomella, E.D. Crawford, L.M. Glode, C.D. Zippe, W.R. Fair, M.E. Marshall, Prostate **20**, 123 (1992)
19. M. Kidwai, V. Bansal, P. Mothsra, S. Saxena, R.K. Somvanshi, S. Dey, T.P. Singh, J. Mol. Catal. A: Chem. **268**, 76 (2007)
20. H. Hagiwara, S. Miya, T. Suzuki, M. Ando, I. Yamamoto, M. Kato, Heterocycles **51**, 493 (1999)
21. H. Hagiwara, N. Fujimoto, T. Suzuki, M. Ando, Heterocycles **53**, 549 (2000)
22. J.N. Sangshetti, N.D. Kokare, D.B. Shinde, Green Chem. Lett. Rev. **2**, 233 (2009)
23. M.H.A. Elgamal, N.M.M. Shalaby, M.A. Shaban, H. Duddeck, B. Mikhova, A. Simon, G. Tóth, Monatsh. Chem. **128**, 701 (1997)
24. W. Li, Y. Wang, Z. Wang, L. Dai, Y. Wang, Catal. Lett. **141**, 1651 (2011)
25. J.M. Khurana, S. Kumar, Monatsh. Chem. **141**, 561 (2010)
26. J.M. Khurana, S. Kumar, Tetrahedron Lett. **50**, 4125 (2009)
27. P. Singh, P. Kumar, R. Chandra, A. Katyal, R. Kalra, S.K. Dass, S. Prakash, Catal. Lett. **134**, 303 (2010)
28. Z.N. Siddiqui, F. Farooq, Catal. Sci. Technol. **1**, 810 (2011)
29. B. Karmakar, A. Nayak, J. Banerji, Tetrahedron Lett. **53**, 4343 (2012)
30. S. Qadir, A.A. Dar, K.Z. Khan, Synth. Commun. **38**, 3490 (2008)
31. W.D. Bossaert, D.E. De Vos, W.M. Van Rhijn, J. Bullen, P.J. Grobet, P.A. Jacobs, J. Catal. **182**, 156 (1999)
32. A. Corma, H. Garcia, Adv. Synth. Catal. **348**, 1391 (2006)
33. M.A. Harmer, W.E. Farneth, Q. Sun, J. Am. Chem. Soc. **118**, 7708 (1996)
34. A.A. Kiss, A.C. Dimian, G. Rothenberg, Adv. Synth. Catal. **348**, 75 (2006)
35. M. Misono, Catal. rev. **29**, 269 (1987)
36. R.A. Sheldon, R.S. Downing, Appl. Catal. A **189**, 163 (1999)
37. A. Vaccari, Appl. Clay Sci. **14**, 161 (1999)
38. D. Margolese, J.A. Melero, S.C. Christiansen, B.F. Chmelka, G.D. Stucky, Chem. Mater. **12**, 2448 (2000)
39. W.M. Van Rhijn, D.E. De Vos, B.F. Sels, W.D. Bossaert, P.A. Jacobs, Chem. Commun. **3**, 317 (1998)
40. D. Das, J.F. Lee, S. Cheng, Chem. Commun. **21**, 2178 (2001)
41. J.G.C. Shen, R.G. Herman, K. Klier, J. Phys. Chem. B. **106**, 9975 (2002)
42. Z. Wang, J.M. Heising, A. Clearfield, J. Am. Chem. Soc. **125**, 10375 (2003)
43. K. Alimohammadi, Y. Sarrafi, M. Tajbakhsh, Monatsh. Chem. **139**, 1037 (2008)
44. Y. Sarrafi, M. Sadatshahabi, K. Alimohammadi, M. Tajbakhsh, Green Chem. **13**, 2851 (2011)
45. Y. Sarrafi, K. Alimohammadi, M. Sadatshahabi, N. Norozipoor, Monatsh. Chem. **143**, 1519 (2012)
46. Y. Sarrafi, E. Mehrasbi, A. Vahid, M. Tajbakhsh, Chin. J. Catal. **33**, 1486 (2012)
47. M. Kruk, M. Jaroniec, Y. Sakamoto, O. Terasaki, R. Ryoo, C.H. Ko, J. Phys. Chem. B. **104**, 292 (2000)