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MCM-41-SO₃H: a novel reusable nanocatalyst for synthesis of amidoalkyl naphthols under solvent-free conditions

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Abstract Nanosized MCM-41-SO₃H based on an ordered mesoporous material with covalently anchored sulfuric acid groups inside the mesochannels was used as an acid catalyst for synthesis of amidoalkyl naphthols in the multicomponent reaction of 2-naphthol, aromatic aldehydes, and an amide. The products were characterized by Fourier-transform infrared (FT–IR), nuclear magnetic resonance (NMR), and mass spectroscopy. The surface area and pore size of MCM-41-SO₃H were also determined by the Brunauer–Emmett–Teller (BET) calculation model. This novel approach for preparation of amidoalkyl naphthols offers several advantages: short reaction times, simple purification and simple isolation of products, high reusability of the catalyst, to name but a few.

Introduction

In recent years, silica mesoporous materials have attracted considerable attention in several scientific areas. Silica materials containing nanopores of constant molecular dimension can be used as heterogeneous catalysts in organic

N. Shadjou Biochemistry Lab, Pasteur Institute of Iran, P.O. Box 13164, Tehran, Iran synthesis. One of the best examples is MCM-41, which is a structurally well-ordered material with a narrow pore size distribution between 1.5 and 10 nm, high surface area up to $1,500 \text{ m}^2 \text{ g}^{-1}$, and thermal stability [1]. It has been demonstrated that Si-MCM-41 has poor Brønsted acid sites and exhibits only weak hydrogen-bonding sites [2, 3] which can be improved via modification of the pore walls by covalent anchoring of different organic or inorganic moieties.

On the one hand several types of solid sulfonic acid have been created in recent years, but on the other hand there have been only a few reports of their application as catalysts in chemical transformations. Regarding our research to develop new and ecofriendly synthetic methodologies towards synthesis of different organic compounds [4-6], we have extended the MCM-41-SO₃H-catalyzed method for synthesis of 1-amidoalkyl-2-naphthol derivatives, which can be converted to important biologically active and druglike molecules such as aminoalkyl naphthols. It is reported that aminoalkyl naphthol derivatives can be prepared by amide hydrolysis of amidoalkyl naphthols [7]. The hypotensive and bradycardic effects of these compounds in normotensive rats as well as their in vitro inotropic and aortic contraction effects in isolated rats' left atria and aorta have been evaluated [8]. Moreover, the intramolecular cyclization of amidoalkyl naphthols produces 1,3-oxazines by the Vilsmeier reagent. These compounds have attracted interest because of their potential as antibiotics, antitumor agents, analgesics, and anticonvulsants [9].

Several efficient methods have been reported for synthesis of amidoalkyl naphthols, employing different acid catalysts such as benzimidazolium-based ionic liquid [10], dodecylphosphonic acid (DPA) [11], Bi(NO₃)₃·5H₂O [12], imidazolium salts [13], MoO₃–ZrO₂ [14], silica chloride [15], Ph₃CCl [16], molten zwitterionic salt [17], H₃Mo₁₂O₄₀P [18], P₂O₅ [19], ferrocene-labeled supported

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ionic liquid phase (SILP) [20], HClO₄–SiO₂ [21, 22], molten tetraethylammonium chloride [23], silica sulfuric acid [24], cation-exchanged resins [25], Fe(HSO₄)₃ [7], and wet cyanuric chloride [26, 27]. Some of these methods suffer from drawbacks such as use of nonreusable and highly acidic catalysts, toxic organic solvents, high temperature, moderate yield, very long reaction time and expensive instruments. Therefore, in this article we introduce a green and efficient procedure based on a nanocatalyst for preparation of the biologically active molecules 1-amidoalkyl-2-naphthols by condensation of β -naphthol, aromatic aldehydes, and an amide using MCM-41-SO₃H (Scheme 1).

Results and discussion

In regard to our research program to develop new and ecofriendly synthetic methodologies towards heterocyclic compounds, herein we disclose a novel, green, rapid and one-pot method for synthesis of amidoalkyl naphthol derivatives catalyzed by MCM-41-SO₃H as heterogeneous nanocatalyst. In the present work, MCM-41 was modified by covalently bonded sulfonic acid on the inside surface of channels to provide the silica-supported material with Brønsted acid properties. MCM-41 was synthesized according to the previously described method [28]. Then, MCM-41 was reacted with chlorosulfonic acid to give a white powder that was named MCM-41-SO₃H. It is notable that not only is the reaction easy and clean, but also no special workup procedure is needed, because HCl gas is released from the reaction vessel immediately (caution: HCl gas is corrosive and precaution is advised) (Fig. 1).

The obtained MCM-41-SO₃H was then characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD), and acid–base titration according to the previous report [5]. Nitrogen absorption and desorption isotherms were obtained at 77 K after the sample was dried at 100 °C for 6 h. Calculations based on the BET plot reveal a high specific surface area of 872.64 m² g⁻¹ and an expected mean pore diameter of 3.2 nm (Fig. 2).



Fig. 1 Preparation of MCM-41-SO₃H



Fig. 2 Plot of BET isotherm

Initially, to illustrate the high efficiency and catalytic activity of MCM-41-SO₃H, in the model reaction 3-nitrobenzaldehyde (1, 1 mmol), β -naphthol (2, 1 mmol), and acetamide (3, 1.2 mmol) were used in the presence of different types of acidic catalyst (Scheme 1).

 Table 1
 Synthesis of N-[(2-hydroxynaphthalen-1-yl)(3-nitrophenyl)

 methyl]acetamide using different catalysts

Entry	Catalyst	Time/min	Yield/%	
1	NaHSO ₄	120	55	
2	SiO ₂	240	30	
3	NaHSO ₄ /SiO ₂	20	78	
4	NH ₄ H ₂ PO ₄ /SiO ₂	30	63	
5	MCM-41-SO ₃ H (0.01 g)	8	80	
6	MCM-41-SO ₃ H (0.02 g)	7	90	
7	MCM-41-SO ₃ H (0.03 g)	6	88	

 Table 2
 Synthesis of N-[(2-hydroxynaphthalen-1-yl)(3-nitrophenyl)

 methyl]acetamide using different amounts of catalyst and reaction conditions

Entry	Condition	Temperature/°C	Time	Yield/%	
1	Solvent free	120	6 min	86	
2	Solvent free	110	7 min	87	
3	Solvent free	100	7 min	90	
4	Solvent free	90	12 min	85	
5	Solvent free	80	15 min	83	
6	CH ₃ OH	Reflux	45 h	20	
7	C ₂ H ₅ OH	Reflux	30 h	40	
8	H_2O	Reflux	48 h	Trace	

As shown in Table 1 (entries 1–5), it was found that MCM-41-SO₃H provides a better acidic condition for this transformation. Meanwhile, it is observed that 0.02 g catalyst shows the best result, while increasing the quantity of the catalyst had no considerable effect on the yield and reaction times. Consequently, 0.02 g was chosen as an optimum amount of catalyst to start the reaction (Table 1, entries 5–7).

To evaluate the effect of solvent and find the optimum reaction temperature, the model reaction was performed under different reaction conditions. The results collected in Table 2 show that 100 °C and solvent-free conditions were the optimum reaction conditions for synthesis of amidoalkyl naphthols **6**.

In the next step, the generality of this procedure catalyzed by MCM-41-SO₃H under the optimum conditions using various aromatic aldehydes containing both electron-donating and electron-releasing groups was examined (Table 3). All of these reactions proceeded smoothly and gave the corresponding products in high yields and short reaction times.

The proposed mechanism for formation of amidoalkyl naphthol is presented in Fig. 3. The reaction occurs inside the pores on the surface of supported sulfonic acid groups which are capable of bonding with the carbonyl oxygen of the aldehyde. Because of hydrogen bonding between carbonyl oxygen and sulfonic acid groups, the electron density of carbonyl decreases, which results in higher susceptibility to nucleophilic attack on carbonyl groups. Nucleophilic addition of 2 to 1 followed by dehydration of its product 4 results in formation of an intermediate named ortho-quinone methide 5. It is well documented that preparation of amidoalkyl naphthols proceeds through the formation of 5, which was introduced by Khodaei et al. [32] for the first time. As is clear from Table 3, electron-withdrawing substituents on an aldehyde increase the reaction rate compared with an aldehyde containing electron-releasing groups. This may be due to lower energy of ortho-quinone methide alkene lowest unoccupied molecular orbital (LUMO) in the presence of electron-withdrawing groups, as Shaterian et al. [33] have declared. Conjunction addition of 3 to 5 led to formation of 1-amidoalkyl-2-naphthol 6.

Reusability of MCM-41-SO₃H

As is known, recycling and reusability is a valuable factor to assess the efficiency and cost-effectiveness of heterogeneous catalysts. We examined the reusability of the catalyst by the reaction of benzaldehyde (5 mmol), β naphthol (5 mmol), acetamide (6 mmol), and catalyst (0.1 g). The recovered catalyst was used in the subsequent reaction after drying at 100 °C. Although some decrease in catalytic activity was observed after four runs (Fig. 4), this can be mainly attributed to errors during filtration, collection, and drying the catalyst that may cause a reduction in the initial amount of used catalyst.

Conclusions

In the current study, a one-pot multicomponent method for synthesis of amidoalkyl naphthol derivatives using MCM-41-SO₃H as an appropriate nanocatalyst was developed. This catalyst is highly efficient, easily available, economical, and requires mild reaction conditions. The innovative aspects of the proposed method are short reaction times omitting toxic solvents or catalyst, very simple work-up procedure, inexpensive starting materials, and improved yield.

Experimental

The physical and spectral data of known products are comparable to corresponding samples prepared via previous method. New products were characterized by IR, ¹H NMR, ¹³C NMR, and mass spectroscopy (MS). Melting points were recorded on a Büchi B-540 apparatus. IR spectra were recorded on an ABB Bomem model FTLA200-100 instrument. ¹H NMR and ¹³C NMR spectra were measured on a

Compound	R^1	\mathbb{R}^2	Time/min	Yield/%	M.p. (lit. m.p.)/°C	References
6a	4	CH ₃	15	86	237-238 (228-229)	[29]
6b	3-NO ₂ -	CH ₃	7	90	240-241 (241-242)	[29]
6c	2,4–Cl ₂ –	CH ₃	12	85	206-208 (198-199)	[29]
6d	4-OH-	CH ₃	20	87	220–221	[30]
6e	4-PhOCH ₂ -	CH ₃	40	75	217–218	_
6f	4-NO ₂ -	CH ₃	15	80	237-239 (248-250)	[21]
6g	4-CH3-	CH ₃	15	86	220.5-222.5 (222-223)	[21]
6h	4-F-	CH ₃	11	88	229-229.5 (209-210)	[29]
6i	H–	CH ₃	10	96	242-243 (241-243)	[29]
6j	4-Br-	CH ₃	18	90	228-230 (228-230)	[31]
6k	2-Cl-	CH ₃	10	90	195–197 (194–196)	[25]
61	4-CN-	CH ₃	9	97	260-262 (261-262)	[26]
6m	3-NO ₂ -	C_6H_5	8	97	227-227.5 (216-217)	[25]
6n	2,4-Cl ₂ -	C_6H_5	8	80	237-237.5 (262-263)	[19]
60	4-PhOCH ₂ -	C_6H_5	10	82	210–212	_
6р	4-NO ₂ -	C_6H_5	8	89	230-231 (228-229)	[19]
6q	4-CH ₃ -	C_6H_5	12	90	204-205 (192-193)	[25]
6r	4-CN-	C_6H_5	15	95	173–174 (176–178)	[26]

Table 3 Preparation of amidoalkyl naphthols 6 catalyzed by MCM-41-SO₃H under solvent-free conditions

Bruker DRX-300 spectrometer at 300 and 75 MHz, using tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported relative to TMS, and coupling constants (*J*) are reported in Hertz (Hz). Nitrogen absorption and desorption isotherms were recorded on BELSORP-max (Japan). Mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer with 70 eV ionization potential.

Synthesis and functionalization of MCM-41

MCM-41 was modified using a 100 cm³ suction flask equipped with a constant pressure dropping funnel containing 81.13 g chlorosulfonic acid (0.7 mol) and a gas inlet tube for conducting HCl gas over an adsorbing solution. Into it was charged 60.0 g MCM-41, and chlorosulfonic acid was then added dropwise over a period of 30 min at room temperature. HCl gas evolved from the reaction vessel immediately, being conducted over the aqueous solution of sodium hydroxide. After completion of addition, the mixture was shaken for 30 min and 115.9 g white solid (MCM-41-SO₃H) was obtained.

General procedure for synthesis of 1-amidoalkyl-2naphthols **6**

A mixture of aldehyde (1 mmol), β -naphthol (1 mmol), acetamide or benzamide (1.2 mmol), and 0.02 g MCM-41-SO₃H was heated in an oil bath at 100 °C for different periods of time (Table 3). After completion of reaction [monitored by thin-layer chromatography (TLC)], the

mixture was cooled to room temperature and excess acetamide or benzamide was washed away by water. The solid was filtered and dissolved in acetone after drying. The catalyst was recovered, and the solution was then concentrated in vacuum to afford crude product. The crystalline pure product was obtained by further recrystallization from EtOH.

N-[(4-Benzyloxyphenyl)(2-hydroxynaphthalen-1-yl)methyl]acetamide (**6e**, C₂₆H₂₃NO₃)

mixture of 0.397 g 4-(benzyloxy)benzaldehyde А (1 mmol), 0.144 g β -naphthol (1 mmol), and 0.070 g acetamide (1.2 mmol) was reacted for 40 min according to the general procedure, affording 0.297 g (75 %) crystalline pure product. M.p.: 217-218 °C; ¹H NMR (300 MHz, acetone- d_6): $\delta = 9.24$ (sbr, 1H, OH), 8.24 (d, J = 8.2 Hz, 1H, NH), 7.94 (d, J = 8.2 Hz, 1H, NCH), 6.87-7.85 (15H, Ar), 5.00 (s, 2H, OCH₂), 1.91 (s, 3H, CH₃) ppm; ¹³C NMR (75 MHz, acetone- d_6): $\delta = 168.7$ (C=O), 158.4, 154.2, 138.4, 135.6, 133.5, 130.3, 130.2, 129.5, 129.2, 128.5, 128.3, 128.2, 127.2, 123.6, 120.6, 119.7, 115.2 (C-Ar), 70.3 (OCH₂), 49.1 (CH), 22.9 (CH₃) ppm; IR (KBr): $\bar{v} = 3,424, 3,286, 3,039, 2,849, 1,668,$ 1,622, 1,514, 1,437, 1,247, 1,190 cm⁻¹; MS (EI): m/z(%) = 396(15), 337(75), 302(81), 269(20), 247(30), 144(30), 115 (25), 91 (85), 65 (50), 43 (75).

N-[(4-Benzyloxyphenyl)(2-hydroxynaphthalen-1-yl)methyl]benzamide (**60**, C₃₁H₂₅NO₃)

A mixture of 0.397 g 4-(benzyloxy)benzaldehyde (1 mmol), 0.144 g β -naphthol (1 mmol), and 0.145 g







Fig. 4 Reusability of MCM-41-SO₃H

benzamide (1.2 mmol) was reacted for 10 min according to the general procedure, affording 0.376 g (82 %) crystalline pure product. M.p.: 210–212 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ = 9.40 (s, 1H, OH), 8.93 (d, *J* = 8.6 Hz, 1H, NH), 8.18 (d, 1H, *J* = 8.6 Hz, NCH), 6.89–7.92 (m, 20H, Ar), 5.05 (s, 2H, OCH₂) ppm; ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 166.7 (C=O), 158.6, 153.8, 138.4, 135.7, 135.3, 133.5, 132.1, 130.4, 130.0, 129.5, 129.3, 129.1, 128.6, 128.5, 128.3, 127.8, 127.7, 123.9, 123.6, 120.1, 119.5, 115.3 (C–Ar), 70.3 (OCH₂), 50.1 (CH) ppm; IR (KBr): $\bar{\nu}$ = 3,409, 3,142, 1,627, 1,540, 1,509 cm⁻¹; MS (EI): *m/z* (%) = 458 (11), 337 (53), 314 (85), 247 (90), 189 (90), 144 (30), 115 (25), 91 (90), 51 (25).

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