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Short Communication

Ultrasound promoted rapid and green synthesis of 1,8-dioxo-octahydroxanthenes derivatives using nanosized MCM-41-SO_3H as a nanoreactor, nanocatalyst in aqueous media

Shahnaz Rostamizadeh [a,*], Ali Mohammad Amani [a], Gholam Hossein Mahdavinia [b], Gelareh Amiri [a], Hamid Sepehrian [c]

[a] Department of Chemistry, KN Toosi University of Technology, P.O. Box 15875-4416, Tehran, Iran
[b] Department of Chemistry, Islamic Azad University–Marvdasht Branch, Marvdasht, Iran
[c] Jaber Ibn Hayan Research Laboratories, Nuclear Science and Technology Research Institute, AEOI, P.O. Box 11365/8486, Tehran, Iran

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ABSTRACT

An efficient and green procedure has been developed for the synthesis of 1,8-dioxo-octahydroxanthenes derivatives. The reaction was carried out in water under ultrasound irradiation, using nanosized MCM-41-SO_3H. In this method, several types of aromatic aldehyde, containing electron-withdrawing groups as well as electron-donating groups, were rapidly converted to the corresponding 1,8-dioxo-octahydroxanthenes in good to excellent yields. This novel synthetic method is especially favored because it provides a synergy of the nanosized MCM-41-SO_3H and ultrasound irradiation which offers the advantages of high yields, short reaction times, simplicity and easy workup compared to the conventional methods reported in the literature.

1. Introduction

Ultrasound process technology is a unique method for the activation and acceleration of processes in chemistry and has been increasingly used in organic synthesis in the last three decades [1–3]. It promotes most types of catalytic processes in chemical syntheses and has a generally accelerating impact on heterogeneous reactions as well as intercalation of guest molecules into host inorganic layered solids. Furthermore, the impetus for ultrasound developments in organic synthesis is the increasing requirement for environmentally clean technology by improving product yields and selectivities, enhancing product recovery and quality through application to crystallization and other product recovery and purification processes [4]. Sonication allows the use of non-activated and crude reagents as well as an aqueous solvent system; therefore, it is eco-friendly and non-toxic. Ultrasound is widely used for improving the traditional reactions that use expensive reagents, strongly acidic conditions, long reaction times, high temperatures, unsatisfactory yields and incompatibility with other functional groups [5].

In recent years more attractive possibilities have been arisen by the development of various new silica materials with ordered structure [6]. one of the best-known examples is MCM-41, which is a structurally well-ordered mesoporous material with a narrow pore size distribution between 1.5 and 10 nm, depending on the surfactant cation and a very high surface area up to 1500 $m^2 g^{-1}$ [7]. It has been proven that Si-MCM-41 lacks Brönsted acid sites and exhibits only weak hydrogen-bonded type sites [8,9]. An additional possibility to develop acidic solids is the modification of the surface of suitable support materials, as the chemical functionalities of these materials can be uniformly modified by covalent anchoring of different organic moieties [10]. While several types of solid sulfonic acids have been created in recent years, there have been only a few reports about their applications as catalyst in chemical transformations. Furthermore, to the best of our knowledge there is no report on the use of these materials as nanocatalysts in the synthesis of 1,8-dioxo-octahydroxanthenes. The obtained nanocatalysts were tested for the synthesis of 1,8-dioxo-octahydroxanthenes under ultrasonic irradiation in aqueous media.

There has been considerable interest in the synthesis of 1,8-dioxo-octahydroxanthens, due to their significant biological activity [11,12]. Some other benzoxanthenes are also utilized in industries as dyes in laser technology [13]. They have also been used in

* Corresponding author. Tel.: +98 21 22853308; fax: +98 21 22853650.
E-mail address: shrostamizadeh@yahoo.com (S. Rostamizadeh).

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photodynamic therapy [14] and are fluorescent materials for visualization of biomolecules [15–18].

Numerous methods have been reported in the literature for the synthesis of 1,8-dioxo-octahydroxanthenes. The classical method involves the condensation of two molecules of dimedone (5,5-dimethyl-1,3-cyclohexanedione) with aromatic aldehydes [19–21], using different catalysts such as *p*-dodecylbenzenesulfonic acid [22], triethylbenzylammonium chloride [23], diammonium hydrogen phosphate under various conditions [24], sulfonic acid under ultrasonic irradiation [25] In this paper, we had the opportunity to further explore the catalytic activity of MCM-41-SO_3H in the synthesis of 1,8-dioxo-octahydroxanthenes.

Herein, we would like to report an efficient route for the synthesis of these compounds from the reaction of readily available and non expensive starting materials of dimedone and an aromatic aldehyde, inside the channels of MCM-41-SO_3H as nanocatalysts under ultrasonic irradiation.

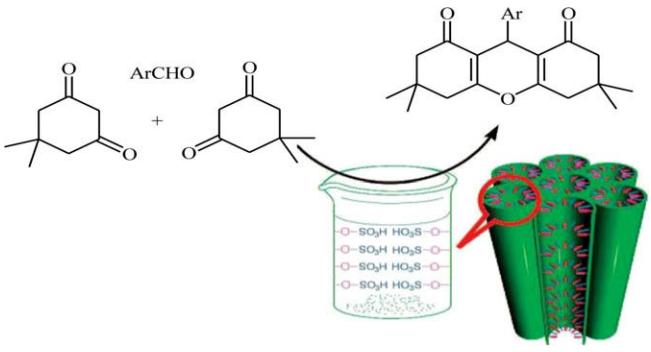
2. Results and discussion

In continuation of our work to develop new and eco-friendly synthetic methodologies [26,27], herein we report a novel, green, facile and efficient one-pot method for the synthesis of 1,8-dioxo-octahydroxanthene derivatives catalyzed by MCM-41-SO_3H as a nanoctalyst under ultrasonic irradiation (Scheme 1).

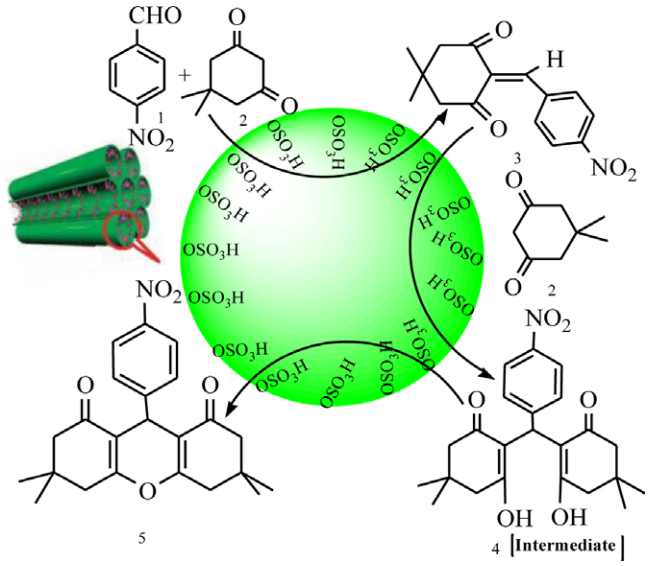
During our investigation, at first, we chose 4-nitrobenzaldehyde and dimedone (mole rate 1:2) under ultrasonic irradiation as model reactants and examined the effect of the amount of MCM-41-SO_3H (Scheme 2, Table 1). According to this data, the optimum amount of catalyst was 0.05 g as shown in Table 1. Further increasing the amount of catalyst did not improve the yield and the reaction time. In order to evaluate the effect of solvent, we examined different solvents under room temperature for the above model reaction (Table 1). The outstanding feature of data that can be elicited from Table 1 is the role of the antihydrophobic property of water in this reaction.

To show the high catalytic activity of MCM-41-SO_3H, the effect of other Lewis acids such as $ZrOCl_2$, $ZrOCl_2$/K10, $NaHSO_4$, $NaHSO_4$/SiO_2 were also investigated in the above model reaction. As shown in Table 1 when the above mixture was reacted under ultrasonic irradiation for 3 h in the presence of these Lewis acids, only the intermediate was detected, which further proves the superior catalytic activity of MCM-41-SO_3H in this transformation. Thus, it is noticeable that the synergy of the nanosized MCM-41-SO_3H and ultrasound irradiation has facilitated this efficient protocol. The combined use of MCM-41-SO_3H and ultrasound is best explained in terms of the intercalation of guest molecules (reactant) into host nanoreactors.

As a matter of fact, localised intense pressure and temperature regions generated by ultrasound help in insertion of reactants toward nanocatalyst channels, and also they accompanied by inherent Brönsted acidity of -SO_3H groups, which are capable of bonding with carbonyl oxygen of the aldehydes, assist in generation of ionic intermediates through activation of reactants, Scheme 2. In other words, ionic intermediates are generated inside the nanoreactor by sufficient energy released during the collapse and strong polarity of the –SO_3H groups. By using this nanocatalyst, the reaction rates and yields under the reaction condition are enhanced, whereas in the presence of mentioned Lewis acids no product is obtained.



Scheme 1.



Scheme 2.

In order to show the effect of ultrasonic irradiation in these reactions, the synthesis of **3i** was investigated as a typical example in the presence of 0, 0.1, 0.2 and 0.05 g of MCM-41-SO_3H with and without ultrasonic irradiation at 60 and 90 °C (Table 2). The reaction rates and yields were dramatically enhanced by ultrasound. The rate enhancement under ultrasound may be attributed to the cavitation, activation of the catalyst and the intercalation of guest molecules into host nanoreactor by sonic waves. In the absence of sonic waves, at 90 °C the products were formed in moderate yields (40–50%) and at 60 °C reaction didn't progress. The role of ultrasound in promoting the rapid and green synthesis of 1,8-dioxo-octahydroxanthenes derivatives is evident from the fact that the corresponding reactions under stirred conditions without ultrasound (silent reactions) needed much longer time for promotion, in all cases with lowered yields (Table 2). Based on the results of this study, it seems that the ultrasound irradiation improves the reaction times and yields.

For a deeper insight in the influence of ultrasound on this work and in order to evaluate the scope and limitations of this work, we focused our attempts on the synthesis of the 1,8-dioxo-octahydroxanthenes using dimedone and benzaldehyde derivatives, the results of which are shown in Table 3. All of the reactions were carried out within 15–90 min and no by-product was observed by TLC analysis. The reaction worked well with electron-withdrawing (NO_2, Cl, CN) as well as electron-donating (Me, MeO) groups, giving various xanthene derivatives in 80–99% yields. As shown in Table 3, the method is general and includes a variety of functional groups.

3. Experimental

Chemicals were obtained from Merck and Sigma–Aldrich and used without further purification. Melting points were recorded

Table 1
The effect of amount of MCM-41-SO_3H, solvent and different catalysts for synthesis of **3b** and **3i**.

Entry	Catalyst[a,b]	Amount of catalyst (g)	Solvent	Time (min)	Yield (%)[c]
1	$ZrOCl_2$[a]	0.1	H_2O	180	Intermediate
2	$ZrOCl_2$/K10[a]	0.3	H_2O	180	Intermediate
3	$NaHSO_4$[a]	0.4	H_2O	180	Intermediate
4	$NaHSO_4/SiO_2$[a]	0.4	H_2O	180	Intermediate
5	MCM-41-SO_3H[b]	0.1	H_2O	60	95
6	MCM-41-SO_3H[b]	0.5	H_2O	60	95
7	MCM-41-SO_3H[a]	0	H_2O	180	Intermediate
8	MCM-41-SO_3H[a]	0.05	H_2O	60	95
9	MCM-41-SO_3H[b]	0.05	H_2O	60	94
10	MCM-41-SO_3H[b]	0.05	Neat	180	Intermediate
11	MCM-41-SO_3H[b]	0.05	EtOH	180	Intermediate

[a] Reaction was performed with 4-nitrobenzaldehyde and dimedone (mole rate 1:2) under ultrasonic irradiation.
[b] Reaction was performed with 4-cyanobenzaldehyde and dimedone (mole rate 1:2) under ultrasonic irradiation.
[c] Isolated yield.

Table 2
Comparison of the amount of catalyst and yields with or without sonication for the synthesis of **3i**.

Entry	MCM-41-SO_3H (g)	With sonication		Without sonication			
		Yield (%)	Time (min)	Yield (%)[a]	Time (min)	Yield (%)[b]	Time (min)
1	0	0	80	0	180	0	180
2	0.2	96	60	50	60	Trace	180
3	0.1	95	60	45	60	Trace	180
4	0.05	95	60	40	60	0	180

[a] Reaction was performed at 90 °C.
[b] Reaction was performed at 60 °C.

Table 3
Preparation of 1,8-dioxo-octahydroxanthenes catalyzed by MCM-41-SO_3H under ultrasonic irradiation.[a,b]

Product	Ar	Time (min)	Yield (%)	Mp (°C)	
				Found	Reported (Lit.)
3a	4-$PhCH_2O$-C_6H_4	15	95	145–147	–
3b	4-CN-C_6H_4	60	94	230	215–217(24)
3c	4-Cl-C_6H_4	60	86	236–237	232–233(24)
3d	2,4-Cl_2-C_6H_4	60	90	248–249	250–252(21)
3e	2-MeO-C_6H_4	60	88	199–200	190–191(19)
3f	4-MeO-C_6H_4	60	95	250–251	241–243(21)
3g	4-MeCONH-C_6H_4	15	96	305–306	305–306(24)
3h	4-Me-C_6H_4	90	99	220–222	218–219(21)
3i	4-NO_2-C_6H_4	60	95	229–230	226–228(22)

[a] The yields refer to the isolated pure products.
[b] The products were characterized from their spectral data (IR, ^1H NMR, ^{13}C NMR and mp) and comparison with literature.

on a Büchi B-540 apparatus and are uncorrected. IR spectra were recorded on an ABB Bomem ModelFTLA200-100 instrument. ^1H and ^{13}C NMR spectra were measured with a Bruker DRX-300 Avance spectrometer at 300 and 75 MHz using TMS as an internal standard. Chemical shifts are reported (δ) relative to TMS, and coupling constants (J) are reported in Hertz (Hz). Mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer with 70 eV ionization potential.

3.1. Synthesis and functionalization of MCM-41

In the present work MCM-41 was modified to covalently anchor sulfonic groups on the inside surface of channels and provide the silica supported material with Brönsted acid properties. The MCM-41 was synthesized according to the previously described method using cetyltrimethylammonium bromide (CTMABr), as the templating agent [28]. The surfactant template was then removed from the synthesized material by calcination at 540 °C for 6 h.

MCM-41 was modified using a 100 mL suction flask equipped with a constant pressure dropping funnel containing chlorosulfonic acid (81.13 g, 0.7 mol) and a gas inlet tube for conducting HCl gas over an adsorbing solution. Into it was charged 60.0 g of 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. After completion of addition the mixture was shaken for 30 min. and the white solid (MCM-41-SO_3H) was obtained (115.9 g).

3.1.1. Characterization

XRD analysis was performed from 1.5° (2θ) to 10.0° (2θ) at a scan rate of 0.02° (2θ)/sec. The XRD patterns after the calcinations of synthesized cerium (IV) silicate samples are presented in Fig. 1. The sample of MCM-41-SO_3H produced relatively well-defined XRD patterns, with one major peak along with three small peaks identical to those of MCM-41 materials [29]. The SEM image of mesoporous MCM-41-SO_3H was taken using 2 min gold coat for high magnification and is shown in Fig. 2.

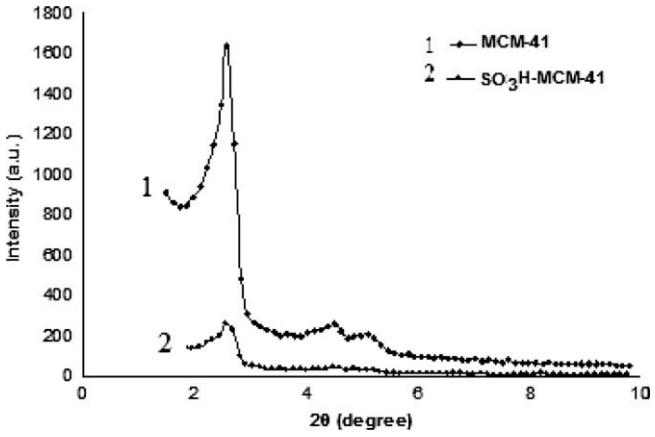


Fig. 1. XRD patterns of MCM-41 and MCM-41-SO_3H.

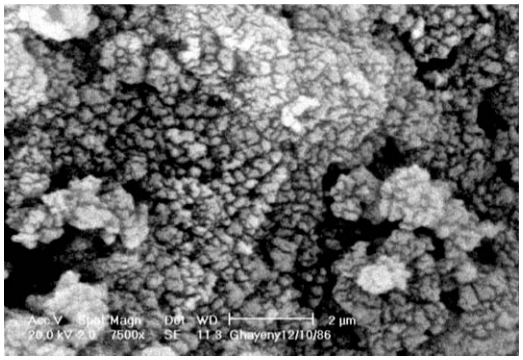


Fig. 2. SEM image of MCM-41-SO_3H.

3.2. Synthesis of 1,8-dioxo-octahydroxanthenes: general procedure

A mixture of aldehyde (1 mmol), dimedone (2 mmol), MCM-41-SO_3H (0.05gr; ~5 mol%, $-SO_3H$ group) and water (5 mL) were mixed and the temperature was then raised to 60 °C and maintained under ultrasonic irradiation (25 kHz) for the appropriate time (Table 3). After completion of the reaction, the water was evaporated and $CHCl_3$ (10 mL) was added and the mixture stirred for at least 10 min. The mixture was filtered and evaporated in *vacuo*, the residues were purified by recrystallization from EtOH.

3.2.1. The spectral data of some representative products

3,3,6,6-Tetramethyl-9-(4-benzyloxyphenyl)-1,8-dioxooctahydroxanthene (Table 3, 3a): IR (KBr, cm^{-1}) V_{max} 3033, 2963, 2871, 1665, 1625, 1604, 1506, 1451, 1359, 1264, 1216, 1196, 1139, 1024, 1001, 840, 738, 696, 606, 535; ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H: 1.00 (6H, s, $2CH_3$), 1.10 (6H, s, $2CH_3$), 2.21 (4H, dd, J_1 = 16.3 Hz, J_2 = 6.7 Hz, $2CH_2$, H-4, H-5), 2.47 (4H, s, $2CH_2$, H-2, H-7), 4.73 (1H, s, H-9), 4.99 (2H, s, CH_2-Bn), 6.85 (2H, d, J = 8.6 Hz, ArH), 7.23 (2H, d, J = 8.6 Hz, ArH), 7.27–7.42 (5H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C: 27.37, 29.28, 30.99, 32.20, 40.84, 50.78, 69.93, 114.34, 115.75, 127.56, 127.85, 128.51, 129.36,136.81,137.23, 157.33, 162.13, 196.49; MS (EI): m/e = 456 (M^+), 365, 321, 273, 217, 91, 77, 41.

3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxooctahydroxanthene (Table 3, 3i): IR (KBr, cm^{-1}) V_{max}: 3040, 2964, 1662, 1619, 1516, 1470, 1363, 1346, 1203, 1168, 1141, 1114, 1004, 870, 836, 694; ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ_H: 0.99 (6H, s, $2CH_3$), 1.12 (6H, s, $2CH_3$), 2.21 (4H, dd, J_1 = 16.4 Hz, J_2 = 6.7 Hz, $2CH_2$, H-4, H-5), 2.49 (4H, s, $2CH_2$, H-2, H-7), 4.82 (1H, s, H-9), 7.46–7.49 (2H, m, ArH), 8.08–8.11 (2H, m, ArH).

References

[1] D.G. Shchukin, H. Möhwald, Phys. Chem. Chem. Phys. 8 (2006) 3496.
[2] D. Peters, J. Mater. Chem. 6 (1996) 1605.
[3] J.T. Li, G.F. Chen, W.Z. Yang, T.S. Li, Ultrason. Sonochem. 10 (2003) 123.
[4] P.W. Cains, P.D. Martin, C. Price, J. Org. Process Res. Develop. 2 (1998) 34.
[5] S.J. Yadav, B.V.S. Reddy, K.B. Reddy, K.R. Raj, A.R. Prasad, J. Chem. Soc. Perkin Trans. 1 (2001) 1939.
[6] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[7] W. Zhang, T.R. Pauly, T.J. Pinnavaia, Chem. Mater. 9 (1997) 2491.
[8] A. Galarneau, D. Desplantier-Giscard, F. Di Renzo, F. Fajula, Catal. Today 68 (2001) 191.
[9] V.Yu. Gusev, X. Feng, Z. Bu, G.L. Haller, J.A. O'Brien, J. Phys. Chem. 100 (1996) 1985.
[10] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, Angew. Chem. Int. Ed. 45 (2006) 3216.
[11] R.W. Lambert, J.A. Martin, J.H. Merrett, K.E.B. Parkes, G.J. Thomas, PCT Int. Appl. WO 9706178, 1997 (Chem. Abstr. 126 (1997) 212377y).
[12] J.P. Poupelin, G. Saint-Rut, O. Foussard-Blanpin, G. Narcisse, G. Uchida-Ernouf, R. Lacroix, Europe. J. Med. Chem. 13 (1978) 67.
[13] S.M. Menchen, S.C. Benson, J.Y.L. Lam, W. Zhen, D. Sun, B.B. Rosenblum, S.H. Khan, M. Taing, US Patent, US 6583168, 2003 (Chem. Abstr. 139 (2003) 54287f).
[14] R.M. Ion, A. Planner, K. Wiktorowicz, D. Frackowiak, Acta Biochim. Pol. 45 (1998) 833.
[15] A. Bekaert, J. Andrieux, M. Plat, Tetrahedron Lett. 33 (1992) 2805.
[16] R.J. Sarma, J.B. Baruah, Dyes Pigm. 64 (2005) 91.
[17] C.A. Buehler, D.E. Cooper, E.O. Scrudder, J. Org. Chem. 8 (1943) 316.
[18] C.G. Knight, T. Stephens, Biochem. J. 258 (1989) 683.
[19] E.C. Horning, M.G. Horning, J. Org. Chem. 11 (1946) 95.
[20] S.J. Tu, J.F. Zhou, Z.S. Lu, X. Deng, D.Q. Shi, S.H. Wang, Synth. Commun. 32 (2002) 3063.
[21] T.-S. Jin, J.-S. Zhang, A.-Q. Wang, T.-S. Li, Synth. Commun. 35 (2005) 2339.
[22] T.S. Jin, J.S. Zhang, J.C. Xiao, A.Q. Wang, T.S. Li, Synlett (2004) 866.
[23] X.-S. Wang, D.-Q. Shi, Y.-L. Li, H. Chen, X.-Y. Wei, Z.-M. Zong, Synth. Commun. 35 (2005) 97.
[24] F. Darvish, S. Balalaei, F. Chadegani, P. Salehi, Synth. Commun. 37 (2007) 1059.
[25] T.-S. Jin, J.-S. Zhang, A.-Q. Wang, T.-S. Li, Ultrason. Sonochem. 13 (2006) 220.
[26] G.H. Mahdavinia, S. Rostamizadeh, A.M. Amani, Z. Emdadi, Ultrason. Sonochem. 16 (2009) 7.
[27] G.H. Mahdavinia, M.A. Bigdeli, M.M. Heravi, Chin. Chem. Lett. 19 (2008) 1171.
[28] H. Sepehrian, R. Yavari, S. Waqif-Husain, M. Ghannadi-Maragheh, Separat. Sci. Technol. 43 (2008) 3269.
[29] J.S. Beck, J.C. Vartulli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B.K. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.