Zirconia-incorporated mesoporous silica nanoparticles as an efficient and reusable catalyst for the synthesis of octahydroxanthene-1,8-diones

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Abstract Zr-containing mesoporous silica with high loading amount of zirconia efficiently catalyzes the reaction of dimedone with aldehydes under solvent-free conditions to afford the corresponding octahydroxanthene-1,8-diones in good-to-excellent yields. Zr-containing mesoporous silica samples with a high loading amount of Zr were prepared by sol–gel method and results show that the catalyst with 20 mol% of Zr has better activity than the catalyst with 10 and 30 mol% of Zr. The catalyst can be recovered and reused with moderate loss of activity.

Keywords Octahydroxanthene-1,8-diones · Zr-MCM-41 · Mesoporous silica · Nanoparticles · Zirconia · Reusability

Introduction

Xanthene derivatives are an important class of heterocyclic compounds because of their useful biological and pharmacological properties such as antiviral, antibacterial, and anti-inflammatory activities [1]. These compounds are also used as luminescent sensors [2], in laser technologies [3], in fluorescent materials for the visualization of biomolecules [4], and in photodynamic therapy [5]. Therefore, the development of a convenient and efficient method for the synthesis of these heterocycles is of practical importance. Several methods for the synthesis of these compounds have been reported. Among them, the general method includes the condensation reaction of aldehydes with dimedone in the presence of acid catalysts.

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A variety of catalysts such as [Hbim]BF₄ [6], $H_3PW_{12}O_{40}/MCM-41$ [7], $HClO_4$ -SiO_2 [8], PPA-SiO_2 [8], Fe³⁺-montmorillonite [9], amberlyst-15 [10], diammonium hydrogen phosphate [11], ZnO nanoparticles [12], starch sulfate [13], and acetic acid [14] are utilized for this condensation reaction. However, the use of many of these catalysts is associated with one or more disadvantages such as long reaction times, low yields, the use of excess reagents/catalysts, harsh reaction conditions, the use of special equipment, and difficulty in recovery and reusability of the catalysts. Hence, there is a need to develop a convenient, efficient, and practically useful protocol for the synthesis of octahydroxanthene-1,8-diones.

In recent years, the use of solid acid catalyst has received considerable attention in organic transformations. This is mainly due to the advantages of solid acid catalysts such as non-toxicity, non-corrosiveness, less expensive, ease of handling, recovery, and reusability [15].

MCM-41 belongs to the family of mesoporous molecular sieves [16] and has been used alone and also in surface or framework-modified form as a catalyst in some organic transformations [17–20]. Some other mesoporous catalysts containing acid/base functionalized sites or mixed oxides were also improved as solid acid catalysts [21–23]. Among the various types of modified MCM-41, zirconia-modified MCM-41 (Zr-MCM-41) has been widely used as a catalyst or catalyst support in some acid-catalyzed reactions [24–26].

In this communication, we wish to report the efficient synthesis of octahydroxanthene-1,8-diones by the reaction of dimedone with aldehydes in the presence of catalytic amounts of zirconia containing mesoporous silica (Zr-MS) as reusable solid acid catalyst (Scheme 1).

Experimental

Materials and methods

All of the chemicals were commercial products. All reactions were monitored by TLC (thin-layer chromatography) and all yields refer to isolated products. Melting points were obtained with a Thermo Scientific-9200 apparatus and are uncorrected. ¹H NMR spectra were recorded in CDCl₃ on a Bruker DRX-500 AVANCE spectrometer. Infrared spectra were recorded on a Shimadzu FT-IR Prestige-21 spectrophotometer in KBr pellets. The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer using nickel-filtered Cu-K α radiation ($\lambda = 1.5406$ Å). Scanning electron micrographs (SEM) were



Scheme 1 Synthesis of octahydroxanthene-1,8-diones in the presence of zirconia incorporated mesoporous silica

obtained on a Philips XL-30 microscope. Transmittance electron microscopy was performed with a Zeiss-EM10C at 80 kV. The BET surface area was performed using a BELSORP instrument (BELSORP-mini JAPAN INC).

Catalyst preparation

The synthesis of zirconia-containing mesoporous silica samples (Zr-MS) was carried out using tetraethylorthosilicate (TEOS) as the Si source, cetyltrimethylammonium bromide (CTAB) as the template, and ammonia as the pH control agent with the gel composition of SiO₂:ZrO₂:CTAB:NH₄OH:H₂O = 1:n:0.115:1.85:460 (n = 0.11 for sample containing 10 mol% Zr, 0.25 for 20 mol% Zr and 0.428 for 30 mol% Zr). In a typical procedure for the synthesis of Zr-MS samples, 0.25 g of CTAB and an appropriate amount of ZrCl₄ (243, 553, and 944 mg for sample containing 10, 20, and 30 mol% of Zr, respectively) dissolved in 50 ml of deionized water at 70 °C; 1.25 g of TEOS was added to above solution for the 20 min. The mixture was further stirred at room temperature for 2 h. A solution of NH₄OH was slowly added into the resulting mixture until a gelatinous solution was obtained, while the pH value of the mixed solution was adjusted to 10.5. The gel was stirred for 24 h and then was centrifuged and washed with distilled water until the supernatant liquid was neutralized. The sample was placed in an oven at 120 °C for 12 h and calcined at 550 °C for 4 h to obtain white-solid Zr-MS samples denoted as 10Zr-MS, 20Zr-MS, and 30Zr-MS, with 10, 20, and 30 mol% loading amount of Zr in the samples, respectively.

General procedure for synthesis of octahydroxanthene-1,8-diones (4a-k)

In a 5-ml round-bottom flask, a mixture of dimedone (2 mmol), aldehyde (1 mmol) and 20Zr-MS (50 mg) was stirred (100 rpm) at 100 °C for 10–85 min. After completion of the reaction (monitored by TLC, eluent; EtOAc:*n*-hexane, 20:80), the mixture was cooled to room temperature and EtOH (15 ml) was added. The resulting solid material was filtered and recrystallized from EtOH/H₂O (2/1) to give the pure product.

Physical and spectroscopic data for selected compound

9-(3-Nitrophenyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione (4 g): Yield: 91 %, white solid, m.p. 191–193 °C (Lit. [23] 163–164 °C); FT-IR: v_{max} (KBr) = 2,960, 1,595, 1,527, 1,377, 1,346 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 0.91 (s, 6H), 1.05 (s, 6H), 2.11 (d, *J* = 12.8 Hz, 2H), 2.29 (d, *J* = 12.0 Hz, 2H), 2.51–2.59 (m, 4H), 4.65 (s, 1H), 7.56 (t, *J* = 6.5 Hz, 1H), 7.70 (d, *J* = 4.0 Hz, 1H), 8.00 (s, 2H) ppm.

Results and discussion

Catalyst characterization

The powder XRD patterns of mesoporous materials usually exhibit the diffraction peaks in the low-angle region. Figure 1 presents the low-angle XRD patterns of the



synthesized MCM-41 and 20Zr-MS samples. As shown in Fig. 1, MCM-41 shows a diffraction peak (100) at 2 θ value of ca. 2.3, and has small and weak diffraction peaks (110 and 200, respectively) at 2 θ value ranging from 4 to 5, which is consistent with hexagonal mesoporous structure of MCM-41 [27]. Figure 1b shows that incorporation of Zr into the MCM-41 framework causes broadening of the main peaks of MCM-41 due to decrease in long-range ordering of the mesostructure of Zr-MS with high loading amount of Zr.

The high-angle XRD patterns of the 20Zr-MS and the nanosized ZrO_2 calcined at 550 °C are shown in Fig. 2. As shown in Fig. 2a, ZrO_2 pattern shows characteristic peaks of both tetrahedral and monoclinic phases. However, absence of these peaks in the Zr-MS pattern (Fig. 2b) confirms that ZrO_2 did not form crystalline phase in the mesoporous silica framework and is dispersed in the framework.

Mesostructure of the 20Zr-MS sample was further studied by TEM, as shown in Fig. 3. Porosity of the sample is clear and disordered mesoporous system is due to the incorporation of Zr into the MCM-41 framework that also confirms by XRD data.

To confirm the presence of Zr in the structure of MCM-41, FT-IR spectra of MCM-41 and 20Zr-MS are shown in Fig. 4. Figure 4a shows main peak of MCM-41 at 459 cm⁻¹ (Si–O-Si bending vibration), 795 cm⁻¹ (Si–O–Si symmetric



Fig. 2 High-angle XRD patterns of the nanosized ZrO₂ (a) and 20Zr-MS (b)



Fig. 3 TEM image of 20Zr-MS

stretching) and $1,100 \text{ cm}^{-1}$ (Si–O–Si asymmetric stretching). In the spectrum of 20Zr-MS (Fig. 4b), broadening of the main peak of silica confirms the presence of Zr in the framework due to overlap of Zr–O bands with this peak.

The SEM image of 20Zr-MS (Fig. 5) shows spherical nanoparticles with the size of <100 nm.

In order to compare the acidic strength of Zr-MS samples, potentiometric titration method was used (Fig. 6). According to this method, the initial potential



Fig. 4 FT-IR spectra of the Zr-MS (a) and MCM-41 (b)



Fig. 5 SEM image of the 20Zr-MS

electrode (E_i) shows the strength of surface acid sites and the range where a plateau is reached (meq/g solid) indicates the total number of acid sites. As shown in Fig. 6, very low initial potential shows that MCM-41 is very weak acid relative to 20Zr-MS

Fig. 6 Potentiometric titration curve of 10Zr-MS (*open circle*), 20Zr-MS (*filled circle*), 30Zr-MS (*filled square*) and MCM-41 (*asterisk*)



Entry	Catalyst	SBET $(m^2 g^{-1})$	
1	MCM-41	900	
2	10Zr-MS	610	
3	20Zr-MS	560	
4	30Zr-MS	350	

Table 1 Surface area of MCM-41 and Zr-MS samples

and 10Zr-MS. However, initial potential of 20Zr-MS is higher and thus has higher acidity strength. The pattern of 30Zr-MS shows lower acidity strength and also lower number of acid sites.

To show the effect of Zr loading on the surface of mesoporous materials, specific surface areas were measured by BET calculation. As shown in Table 1, surface area was decreased by the incorporation of Zr onto the framework of silica from 610 to 350 with increase in Zr loading. Although, according to acidity measurement results, 20Zr-MS shows the better catalytic activity, this is not in contrast with the results of BET. The lower acidity in 10Zr-MS sample may be due to lower loading of Zr and also lower acidity of 30Zr-MS may be due to serious reduction of surface and also mesoporosity because of very high incorporation of Zr onto the silica framework.

Catalyst activity

Initially, the reaction of dimedone and benzaldehyde was selected as the model reaction for optimization experiments and results are summarized in Table 2. To optimize the effect of Zr/Si mole ratio on the catalytic activity of Zr-MS, the model reaction was performed in the presence of Zr-MS prepared by different Zr/Si mol%. As shown in Table 2, the catalyst activity was increased by increase in the amount of Zr from 10 up to 20 % and then was decreased after increase in amount of Zr up to 30 %. The results show that 20Zr-MS has the best activity in term of reaction time and yield of the product (Table 2, entry 2). This is in agreement with the obtained results of acid strength by potentiometric titration. To optimize the amount of the catalyst, the model reaction was carried out in the presence of various amounts of 20Zr-MS (Table 2, entries 2, 4, 5) and results show that the use of 100 mg catalyst for 1 mmol of aldehyde has the best results. To show efficiency of Zr in the framework of silica, the model reaction was also carried out in the presence of 100 mg MCM-41 and ZrO₂. The results show low activity for these catalysts (Table 2, entries 6, 7).

Following the obtained results, the reaction of dimedone and benzaldehyde was carried out in the presence of 100 mg of 20Zr-MS in solvent-free conditions at 100 °C and the corresponding octahydroxanthene-1,8-diones was obtained in 90 % yield (Table 3, entry 3a). The scope and generality of this method was investigated in the reaction of various types of aldehydes with dimedone. Aldehydes with both electron-donating and electron-withdrawing substituents were reacted with dimedone at the same reaction conditions and the corresponding octahydroxanthene-1,8-diones were obtained in the 80-92 % yields (Table 3, entries 3b-k).

To investigate reusability of the catalyst, the recovered catalyst from the model reaction (run 1, Table 4), was washed with EtOH and dried at 120 °C and then reused at the same reaction conditions (run 2, Table 4). This was repeated for a third run. The results show a moderate decrease in activity after recovering. This may be due to partial blocking of active sites of the catalyst in the reaction media and/or partial leaching of nanoparticles. In order to clean the surface of the active sites, the

Entry	Catalyst	Catalyst amount (mg)	Substrate:Zr (molar ratio)	Time (min) ^a	Yield (%) ^b
1	10Zr-MS	100	0.13	180	75
2	20Zr-MS	100	0.21	40	90 ^c
3	30Zr-MS	100	0.27	145	80
4	20Zr-MS	75	0.16	100	81
5	20Zr-MS	50	0.11	135	81
6	MCM-41	100	-	35	72
7	ZrO_2	100	0.43	28	76

Table 2 Optimization of the catalyst condition in the reaction of benzaldehyde and dimedone

^a Time of complete conversion of reactant or stop of reaction

^b Isolated yield

^c TON and TOF was obtained 3.34 and 5 h⁻¹, respectively

Table 3Synthesis ofoctahydroxanthene-1,8-diones inthe presence of 20Zr-MS at100 °C under solvent-freeconditions

Entry	Aldehyde (1)	Product (3)	Time (min)	Yield ^a (%)
a	O H		40	90
b	CI H		65	87
с	CI U H		30	80
d	Cl O H		25	87
e	но		10	92
f	F N		35	88
g	NO ₂		70	91
h	O ₂ N H		85	85
i	MeO		40	81
j	Me		60	80
k	MeO H	OMe OMe	60	84

Reaction conditions: aldehyde (1 mmol), dimedone (2 mmol),

^a Isolated yields

(1 minor), dimedone (2 minor), 20Zr-MS (100 mg), substrate:Zr molar ratio: 0.27, temp. (100 °C)

recycled catalyst after the third run was calcined at 300 °C for 4 h. Then again, the catalyst was used in the model reaction. Enhancement in the activity after calcination of recovered catalyst confirms that some of the deactivation is due to partial blockage of active sites of the catalyst (run 4, Table 4). It should be noted that at 300 °C the calcination may be incomplete and partial blockage may remain. To investigate leaching, the model reaction was carried out using fresh catalyst and

Table 4 Reusability of 20Zr-MS in the reaction ofbenzaldehyde and dimedone	Run	Time (min)	Yield (%)
	1	40	90
	2	45	80
	3	50	79
	4	45	86

Table 5 Comparison of 20Zr-MS with other catalysts for the synthesis of octahydroxanthene-1,8-diones

Entry	Catalyst	Solvent	Condition	Time (min.)	Yield (%)
1	20Zr-MS	_	90 °C	40	90 [this work]
2	[Hbim]BF4	_	Ultrasound	45	85 [<mark>6</mark>]
3	H ₃ PW ₁₂ O ₄₀ /MCM-41	EtOH	90 °C	300	94 [7]
4	HClO ₄ -SiO ₂	_	140 °C	30	32 [8]
5	PPA-SiO ₂	_	140 °C	30	93 [<mark>8</mark>]
6	Fe ³⁺ -montmorillonite	EtOH	100 °C	360	94 [<mark>9</mark>]

after 10 min the reaction was stopped by cooling to r.t. and then the catalyst was filtered by dilution with EtOH. The solvent was evaporated at low temperature and the reaction was continued at 100 $^{\circ}$ C (without catalyst). Slight progress of the reaction may be due to presence of trace amounts of leached nanoparticles in the reaction media.

Reactivity of 20Zr-MS was compared with other reported catalysts for the synthesis of octahydroxanthene-1,8-diones (Table 5). With an overall look at Table 5, we can say that our method is comparable with other catalytic systems in terms of yield and reaction time. In addition to this, reusability and absence of solvent are some obvious benefits with respect to the other mentioned catalysts.

Conclusions

In this work, we reported a modified simple method for the preparation of Zr-MCM-41 and its application as catalyst for the synthesis of octahydroxanthene-1,8-diones. The reusability, solvent-free conditions, simple workup, and non-toxicity of the catalyst are some advantages of the method.

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References

- 1. J. Poupelin, G. Saint-Rut, O. Fussard-Blanpin, G. Narcisse, G. Uchida-Ernouf, R. Lakroix, Eur. J. Med. Chem. 13, 67 (1978)
- 2. J.F. Callan, A.P. de Silva, D.C. Magri, Tetrahedron 61, 8551 (2005)

- O. Siirkecioglu, N. Talini, A. Akar, M. Ahmad, T. King, D. Ko, B. Cha, J. Lee, J. Chem. Res. Synop. 35, 502 (1995)
- 4. C.G. Knight, T. Stephens, Biochem. J. 258, 683 (1989)
- R.-M. Ion, A. Planner, K. Wiktorowicz, D. Frackowiak, Acta Biochim. Pol.English Edition 45, 833 (1998)
- 6. K. Venkatesan, S.S. Pujari, R.J. Lahoti, K.V. Srinivasan, Ultrason. Sonochem. 15, 548 (2008)
- 7. G. Karthikeyan, A. Pandurangan, J. Mol. Catal. A Chem. 311, 36 (2009)
- 8. S. Kantevari, R. Bantu, L. Nagarapu, J. Mol. Catal. A Chem. 269, 53 (2007)
- 9. G. Song, B. Wang, H. Luo, L. Yang, Catal. Commun. 8, 673 (2007)
- 10. B. Das, P. Thirupathi, I. Mahender, V.S. Reddy, Y.K. Rao, J. Mol. Catal. A Chem. 247, 233 (2006)
- 11. F. Darviche, S. Balalaie, F. Chadegani, P. Salehi, Synth. Commun. 37, 1059 (2007)
- 12. Z. Lasemi, E. Mehrasbi. Res. Chem. Intermed. (2013). doi:10.1007/s11164-013-1394-7
- 13. H. R. Shaterian, F. Rigi, Res. Chem. Intermed. (2013). doi:10.1007/s11164-013-1223-z
- N. Hazeri. A. Masoumnia. M. T. Mghsoodlou. S. Salahi. M. Kangani. S. Kianpour. S. Kiaee, J. Abonajmi, Res. Chem. Intermed. (2014). doi:10.1007/s11164-013-1516-2
- 15. M. Abdollahi-Alibeik, M. Pouriayevali, React. Kinet. Mech. Catal. 104, 235 (2011)
- 16. C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359, 710 (1992)
- 17. M. Abdollahi-Alibeik, M. Pouriayevali, Catal. Commun. 22, 13 (2012)
- 18. M. Abdollahi-Alibeik, E. Heidari-Torkabad, C. R. Chim. 15, 517 (2012)
- 19. P. Iliade, I. Miletto, S. Coluccia, G. Berlier, Res. Chem. Intermed. 38, 785 (2011)
- 20. J.-K. Jeon, Y.-K. Park, J.-H. Yim, Res. Chem. Intermed. 36, 661 (2010)
- 21. N.R. Shiju, A.H. Alberts, S. Khalid, D.R. Brown, G. Rothenberg, Angew. Chem. 123, 9789 (2011)
- 22. J. Dulle, K. Thirunavukkarasu, M.C. Mittelmeijer-Hazeleger, D.V. Andreeva, N.R. Shiju, G. Rothenberg, Green Chem. 15, 1238 (2013)
- P.D. Carà, M. Pagliaro, A. Elmekawy, D.R. Brown, P. Verschuren, N.R. Shiju, G. Rothenberg, Cat. Sci. Tech. 3, 2057 (2013)
- 24. K. Bachari, R. Chebout, R.M. Guerroudj, M. Lamouchi, Res. Chem. Intermed. 38, 367 (2011)
- 25. Y.C. Chien, H.P. Wang, S.H. Liu, T.L. Hsiung, H.S. Tai, C.Y. Peng, J. Hazard. Mater. 151, 461 (2008)
- L.F. Chen, L.E. Norena, J.A. Wang, X.L. Zhou, J. Navaffete, I. Hernandez, A. Montoya, P.P. Romo, P. Salas, S.C. Pergher, Catal. Today 133, 331 (2008)
- 27. M. Abdollahi-Alibeik, F. Nezampour, React. Kinet. Mech. Catal. 108, 213 (2013)