IAU-ARAK

J. Iran. Chem. Res. 3 (2010) 117-120

Journal of the Iranian Chemical Research

www.iau-jicr.com

MCM-41 functionalized sulfonic acid catalyzed one-pot synthesis of 1,8-dioxo-octahydroxanthenes

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Received 30 January 2010; received in revised form 25 May 2010; accepted 30 May 2010

Abstract

MCM-41-R-SO_3H catalyzed one-pot synthesis of 1,8-dioxo-octahydroxanthenes is reported under reflux conditions. The catalyst is easily prepared, highly stable, very simple to handle and recycled for five times without loss of significant activity

Keywords: One-pot; MCM-41-R-SO_3H; Heterogeneous; Hydroxanthene; Multicomponent.

1. Introduction

Heterogeneous solid acid catalysts for the synthesis of fine chemicals have attracted considerable attention from both environmental and economical perspectives. Recently, more emphasis is made on solid acids containing organic-inorganic hybrids in which acid functionality is covalently anchored onto inorganic support. These solid acids find increased advantages such as easy separation from the reaction medium; reactions are usually clean and selective, procedures are usually cost-effective, and the catalyst is stable and hence can be recycled, which leads to high turn-over numbers. The organic tailoring of the internal surface of mesoporous materials has recently received great attention in terms of the application of such materials in the fields of catalysis. In recent times more attractive possibilities arose by the development of various new silica materials with ordered structure [1] one of the best-known examples is MCM-41, which is a structurally well-ordered mesoporous material with narrow pore size distribution between 1.5 and 10 nm, depending on the surfactant cation and a very high surface area up to 1500m^2 g^{-1}[2].

It has been proved that Si-MCM-41 lacks Brönsted acid sites and exhibits only weak hydrogen-bonded type of sites [3]. Among various covalently anchored solid acids, MCM-41 functionalized sulfonic acid (MCM-41-R-SO_3H) finds more utility in organic synthesis [4]. There has been considerable interest in the synthesis of 1,8-dioxo-octahydroxanthens, due to their significant biological activity [5]. Some other benzoxanthenes are also utilized in industries as dyes in laser technology. They have also been used in photodynamic therapy [6] and are fluorescent materials for visualization of biomolecules [7].

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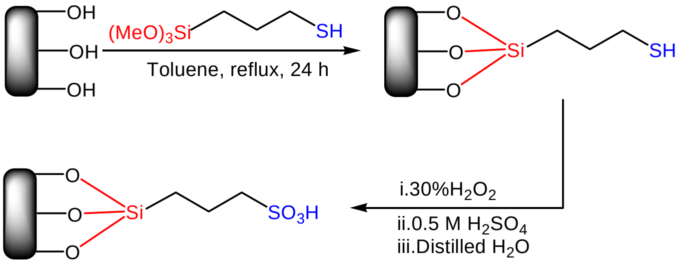
Numerous methods have been reported in the literature for the synthesis of 1,8-dioxo-octahydroxanthenes. The classical method involves the condensation of two molecules of 5,5-dimethyl-1,3-cyclo-hexanedione with aromatic aldehydes, using different catalysts such as *p*-dodecylbenzenesulfonic acid [8], triethylbenzylammonium chloride [9], diammonium hydrogen phosphate under various conditions [10], sulfonic acid under ultrasonic irradiation [11]. 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 5,5-dimethyl-1,3-cyclo-hexanedione and an aromatic aldehyde, inside the channels of MCM-41-R-SO_3H as nanocatalysts. The preparation procedure for catalyst MCM-41-R-SO_3H is outlined in Scheme 1 with slight modification than the already reported method.



Scheme 1

2. Experimental

2.1. Synthesis of 3-mercaptopropyl MCM-41 (MPMCM-41)

The MCM-41 (5 g) was added to a solution of 3-mercaptopropyl (trimethoxy)silane (10 mmol) in dry toluene and refluxed for 24 h. The 3-mercaptopropyl MCM-41 (MPMCM-41) was filtered off and washed with hot toluene and dried at 110 °C for 5 h to give the surface bound thiol (MPMCM-41) groups.

2.2. Synthesis of covalently anchored sulfonic acid onto MCM-41 (MCM-41-R--SO_3H)

The mixture of 3-mercaptopropyl MCM-41 (MPMCM-41, 5 g), 30 % H_2O_2 solution (50 mL) and conc. H_2SO_4 (0.078 g, 0.8 mmol) was stirred at room temperature for 20h. The solid was filtered off at pump and washed with excess distilled water till the washings were neutral. In order to confirm that all the sulfonic acid groups are protonated, the solid material was further suspended in 0.05 M H_2SO_4 (30 mL) for 5h. The solid was then filtered off and washed with excess distilled water till the washings were neutral. Finally it was dried in air at 110 °C for 5h.

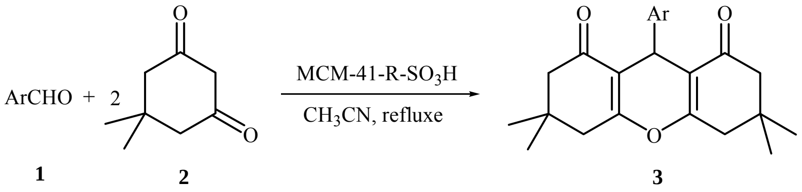
2.3. General procedure for the synthesis of 1,8-dioxo-octahydroxanthenes

A solution of 1 mmol of aldehyde and 2 mmol of dimedone in CH_3CN (5mL), was added the MCM-41-R--SO_3H (0.1 g) in a 20 mL glass vial. The mixture was refluxed for an appropriate time according to Table **1.** The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by simple filtration. Then solvent was evaporated and the solid was crystallized by ethanol.

3. Results and discussion

The presence of covalently anchored organic functionality onto the surface of MCM-41 was determined by thermogravimetric analysis (TGA). The TGA curve shows the initial weight loss below 100 °C, which is attributed to residual solvent or water molecules trapped into the MCM-41 framework, then the subsequent weight loss occurs between 260 to 550 °C, which is because of the loss of organic functionalities covalently anchored onto the surface of MCM-41. Typically, a loading of 1.13 mmol g^{-1} was obtained, which was based on the determination of sulfur content by the elemental analysis and acid-base titrations. A loading of 1.10 mmol g^{-1} was obtained for the recoverd catalyst by acid-base titrations.

In order to achieve the optimum conditions, the reaction of 4-nitrobenzaldehyde and dimedone (mole rate 1:2) were selected as the model. The effects of amount of catalyst (1-5 mol %), different solvents (none, methylene chloride, toluene and acetonitrile) and different temperatures (r.t., 60, 80 °C and reflux) were examined. The results were evaluated qualitatively through TLC. The best conditions employ 0.1g of the catalyst at reflux condition for 20-30min using acetonitrile as solvent. Using optimized conditions, the reaction of various aromatic aldehydes and dimedone were investigated (Scheme 2).



Scheme 2

It was found that all the reactions proceeded smoothly to give the corresponding 1,8-dioxo-octahydroxanthenes in high yields (Table 1). Both aromatic aldehydes bearing electron-donating groups and electron-withdrawing groups gave excellent yields. The results are summarized in Table 1, which clearly indicate the generality and scope of the reaction with respect to various aromatic aldehydes.

In order to verify whether the reaction was catalyzed by catalyst MCM-41-R-SO_3H or with silica gel used for preparing the catalyst, we have carried out the reaction (in case of product entry 3) without using any catalyst as well as using activated silica gel (0.1 g) under similar conditions as with catalyst MCM-41-R-SO_3H. It was found that product was formed in traces (as observed on TLC) when silica gel was used solely in 2 h.

In conclusion, we have developed a mild, simple, cost-effective for the synthesis of 1,8-dioxo-octahydroxanthenes using reusable covalently anchored sulfonic acid onto the surface of MCM-41 solid acid catalyst as nanocatalyst under heterogeneous catalysis conditions. Moreover, the mild reaction conditions, high yield of products, easy work-up, ready availability of the catalyst, compatibility with various functional groups and the ecologically clean procedure, will make the present method a useful and important addition to the present methodologies for this synthesis.

Table 1
Preparation of 1,8-dioxo-octahydroxanthenes **3** catalyzed by MCM-41-R-SO_3H under reflux conditions.

Entry	Ar	Time (min)	Yield (%)	Product	Mp (°C)
1	C_6H_5	20	94	**3a**	204-205
2	4-ClC_6H_4	20	94	**3b**	225-226
3	2-ClC_6H_4	20	85	**3c**	228-230
4	4-BrC_6H_4	20	94	**3d**	233-235
5	4-FC_6H_4	20	96	**3e**	224-225
6	4-MeC_6H_4	25	92	**3f**	218-220
7	4-$MeOC_6H_4$	25	90	**3g**	243-245
8	2-$MeOC_6H_4$	30	85	**3h**	184-185
9	3-$MeOC_6H_4$	30	85	**3i**	177-180
10	2,4-$MeOC_6H_3$	30	90	**3j**	209-211
11	4-OHC_6H_4	25	85	**3k**	243-245
12	2-OHC_6H_4	30	82	**3l**	202-205
13	4-$NO_2C_6H_4$	20	95	**3m**	226-227
14	3-$NO_2C_6H_4$	20	93	**3n**	168-170
15	$C_6H_5CH=CH$	25	90	**3o**	177-178
16	2-Naphthyl	20	92	**3p**	194-196

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