

## Magnetically separable modified sulfuric acid ( $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ ): Preparation, characterization and catalytic application for the synthesis of 1, 8-dioxo-octahydroxanthenes

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### Abstract

A nanomagnetic acidic catalyst ( $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ ) was prepared by the chemical anchoring of sulfuric acid onto the surface of modified  $\text{CuFe}_2\text{O}_4$  magnetic nanoparticles and characterized using FT-IR, SEM, EDX, and VSM techniques. The results confirmed that the sulfuric acid is well dispersed on the surface of the nanomagnetic support. The catalytic activity of  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  was evaluated in the synthesis of 1, 8-dioxo-octahydroxanthenes under solvent-free conditions. The reactions using this nanomagnetic acidic catalyst could be carried out in lower than 12 min with excellent yields. Also, the catalyst was easily isolated from the reaction mixture by an external magnet and used at least four times without significant loss of activity.

**Keywords:** Magnetic nanoparticles;  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ ; 1, 8-Dioxo-octahydroxanthenes; heterogeneous catalyst; solvent-free conditions.

### Introduction

Xanthene derivatives, in particular xanthenediones, have received significant attention because they are parent structures of great number of naturally occurring compounds. They include a number of biological properties such as antibacterial [1], antiviral [2], anti-inflammatory [3], phototoxicity [4], antiproliferative [5], and anticancer [6]. Furthermore, they are well-known as fluorescent and laser dyes [7-9]. Xanthenediones are generally synthesized by condensation of aromatic aldehydes with 1, 3-cyclohexanedione or 5, 5-dimethyl-1, 3-cyclohexanedione

(dimedone) using various promoting agents such as sulfated zirconia [10], multiwalled carbon nanotube-supported butyl 1-sulfonic acid (MWCNT-BuSO<sub>3</sub>H) [11],  $\beta$ -cyclodextrin grafted with butyl sulfonic acid ( $\beta$ -CD-BSA) [12], ceric ammonium nitrate supported HY-zeolite (CAN/HY-zeolite) [13], silica-supported Preyssler nano particles (Silica/Preyssler NPs) [14], L-proline [15], ZnO nanoparticles [16], SmCl<sub>3</sub> [17], nanosized MCM-41-SO<sub>3</sub>H [18], trimethylsilyl chloride [19], H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/MCM-41 [20], and [Et<sub>3</sub>NC<sub>4</sub>SO<sub>3</sub>H][HSO<sub>4</sub>]/Al<sub>2</sub>O<sub>3</sub> [21]. Some of these catalysts have disadvantages

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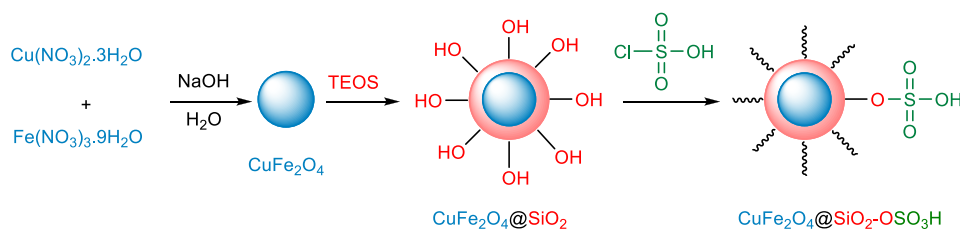
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such as low yields, prolonged reaction times, harsh reaction conditions, requirement of excess of catalyst, and the use of toxic organic solvents. Thus, the development of an alternate clean procedure using efficient catalyst is highly demanding for the synthesis of 1,8-dioxo-octahydroxanthenes, which surpasses those limitations.

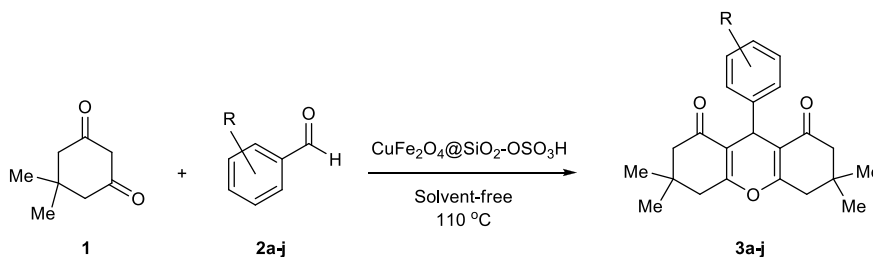
Catalysts and catalytic reactions have attracted great attention in industrial applications and basic researches [22-25]. With increasing environmental concerns, the development of clean synthetic procedures has been widely studied. Most of the homogeneous catalysts have high activity and selectivity [26,27], however, heterogeneous ones can be easily handled, separated and reused. The potential advantage of heterogeneous catalysts allows the development of environmentally benign processes in both academic and industrial environment [28, 29]. In recent years, among the various heterogeneous catalysts, magnetic nanoparticles (MNPs) with high surface area and their unique magnetic properties [30] have

been widely applied in various chemical reactions [31-37]. They are separated from the reaction medium by an external permanent magnet. The MNPs containing acidic functional groups, especially SO<sub>3</sub>H-functionalized, have become crucial and demanding researches and are suitable substitute catalysts for conventional acids such as H<sub>2</sub>SO<sub>4</sub>, HF and AlCl<sub>3</sub> in chemical processes [38-40].

In this view and in line with our interest in the application of reusable catalysts in organic reactions [41-47] and in continuation of our previous works in the synthesis of new MNPs [48,49], we report the preparation of SO<sub>3</sub>H-functionalized magnetic core-shell nanoparticles, CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-OSO<sub>3</sub>H, by coating a SiO<sub>2</sub> shell around CuFe<sub>2</sub>O<sub>4</sub> MNPs followed by immobilization of sulfuric acid (Scheme 1). The catalytic activity of the prepared heterogeneous and green acidic magnetic nanocatalyst was tested in the synthesis of 1,8-dioxo-octahydroxanthenes **3a-j** by the reaction of aromatic aldehydes **2a-j** with dimedone **1** under solvent-free conditions (Scheme 2).



**Scheme 1.** Preparation of CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-OSO<sub>3</sub>H MNPs



**Scheme 2.** Synthesis of 1,8-dioxo-octahydroxanthenes in the presence of CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-OSO<sub>3</sub>H MNPs

## Experimental

All chemicals were purchased from Merck and Aldrich and used without further purification. Melting points were recorded with a Stuart SMP3 melting point apparatus. The  $^1\text{H}$  NMR (300 MHz) spectra were recorded on a Bruker 300 FT spectrometer, in  $\text{CDCl}_3$  as the solvent using tetramethyl silane (TMS) as internal standard. Fourier transform infrared (FT-IR) spectra were obtained using a Tensor 27 Bruker spectrophotometer at KBr disks. Ultrasonication was performed using a Soltec sonicator at a frequency of 40 kHz and a nominal power of 260 W. Scanning electron microscopy (SEM) analysis was done using a MIRA3 TESCAN scanning electron microscope operated at an accelerating voltage of 30 kV. Energy-dispersive X-ray (EDX) analysis was performed using a SAMX model instrument. Magnetization curves were obtained with a MDKFT vibrating sample magnetometer (VSM).

### *Preparation of $\text{CuFe}_2\text{O}_4$ MNPs*

$\text{CuFe}_2\text{O}_4$  MNPs were precipitated in water in the presence of sodium hydroxide solution of  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Fe}(\text{NO}_3)_3$  [50]. Typically,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (2.02 g, 5 mmol) and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.60 g, 2.5 mmol) were dissolved in water (10 mL), and aqueous NaOH (4 M, 30 mmol, 7.5 mL) was added at room temperature over a period of 10 min to form a reddish-black precipitate. The reaction continued for 2 h at 90 °C. After cooling to room temperature, magnetic particles were collected by a magnetic separator, washed with water ( $3 \times 10$  mL) and kept in an air oven overnight at 80 °C. The resulting particles were finally ground with a pestle and mortar and kept in a furnace at 800 °C for 4 h and then slowly cooled to room temperature to form  $\text{CuFe}_2\text{O}_4$  MNPs.

### *Preparation of silica-coated $\text{CuFe}_2\text{O}_4$ MNPs ( $\text{CuFe}_2\text{O}_4@\text{SiO}_2$ )*

The core/shell  $\text{CuFe}_2\text{O}_4@\text{SiO}_2$  was prepared according to the literature procedure [51]. The  $\text{CuFe}_2\text{O}_4$  MNPs (2.0 g, 8.5 mmol) were ultrasonically dispersed in ethanol (25 mL) for 15 min at room temperature and then 25% aqueous ammonia (10 mL) was added to the mixture and stirred at 60 °C for 40 min followed by the addition of tetraethyl orthosilicate (TEOS, 1.0 mL) which was drop wise added to this mixture and stirring was continued at the same temperature for 24 h. The obtained  $\text{CuFe}_2\text{O}_4@\text{SiO}_2$  MNPs were separated by a permanent magnet and washed repeatedly with methanol ( $3 \times 5$  mL) and dried in vacuum at 50 °C for 48 h. The resulting  $\text{CuFe}_2\text{O}_4@\text{SiO}_2$  MNPs were then calcined at 800 °C for 4 h.

### *Preparation of silica sulfuric acid coated $\text{CuFe}_2\text{O}_4$ MNPs ( $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ )*

Chlorosulfonic acid (0.52 g, 4.5 mmol) was added in a drop-wise manner to a cooled (ice-bath) solution of  $\text{CuFe}_2\text{O}_4@\text{SiO}_2$  (1 g) in *n*-hexane (5 mL) over a 2 h period. Upon completion of the addition, the mixture was stirred for a further 3 h until to allow for the complete dissipation of HCl from the reaction vessel. The resulted MNPs were separated using an external magnet and washed with methanol before being dried in an oven at 60 °C to give  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  as a brown powder. The amount of  $\text{H}^+$  in the  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  determined by acid-base potentiometric titration using NaOH as titrant was 2.81 mmol/g.

### *General procedure for synthesis of 1,8-dioxo-octahydroxanthenes (3a-j) catalyzed by $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ MNPs*

Preparation of 1, 8-dioxo-octahydroxanthenes was typically

performed according to the following procedure. The catalyst,  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ , (0.04 g) was added to a mixture of dimedone **1** (2.0 mmol) and an aromatic aldehyde **2a-j** (1.0 mmol). The mixture was heated in an oil bath at 110 °C for 8-12 min and monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and hot acetone (15 mL) was added. The catalyst was separated by external magnet. The solvent was evaporated *in vacuo* and the residue was recrystallized from ethanol to afford compounds **3a-j** in high yields.

*9-(4-Chlorophenyl)-3, 3, 6, 6-tetramethyl-1, 8-dioxo-octahydroxanthene (3a)*.  $^1\text{H}$  NMR ( $\delta$ , ppm): 1.13 (s, 6H, 2CH<sub>3</sub>), 1.24 (s, 6H, 2CH<sub>3</sub>), 2.30-2.55 (m, 8H, 4CH<sub>2</sub>), 5.50 (s, 1H, CH), 7.04 (d,  $J = 8.1$  Hz, 2H, arom-H), 7.25 (d,  $J = 8.1$  Hz, 2H, arom-H);  $^{13}\text{C}$  NMR ( $\delta$ , ppm): 27.3, 29.3, 31.5, 32.2, 40.8, 50.7, 115.3, 128.2, 129.8, 132.0, 142.7, 162.5, 196.4; FT-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2952, 1661, 1625, 1489, 1469, 1413, 1361, 1198, 1166, 1140, 1089, 1003, 852.

*9-(2-Chlorophenyl)-3, 3, 6, 6-tetramethyl-1, 8-dioxo-octahydroxanthene (3b)*.  $^1\text{H}$  NMR ( $\delta$ , ppm): 1.04 (s, 6H, 2CH<sub>3</sub>), 1.12 (s, 6H, 2CH<sub>3</sub>), 2.13-2.29 (m, 4H, 2CH<sub>2</sub>), 2.47 (s, 4H, 2CH<sub>2</sub>), 5.02 (s, 1H, CH), 7.08 (t,  $J = 6.9$  Hz, 1H, arom-H), 7.19 (t,  $J = 7.2$  Hz, 1H, arom-H), 7.24 (d,  $J = 7.8$  Hz, 1H, arom-H), 7.45 (d,  $J = 7.2$  Hz, 1H, arom-H); FT-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3070, 2960, 1664, 1625, 1468, 1356, 1203, 1156, 1036, 1006, 840, 793.

*9-(4-Nitrophenyl)-3, 3, 6, 6-tetramethyl-1, 8-dioxo-octahydroxanthene (3d)*.  $^1\text{H}$  NMR ( $\delta$ , ppm): 0.91 (s, 6H, 2CH<sub>3</sub>), 1.04 (s, 6H, 2CH<sub>3</sub>), 2.09 (d,  $J = 16.5$  Hz, 2H, CH<sub>2</sub>), 2.18 (d,  $J = 16.2$  Hz, 2H, CH<sub>2</sub>), 2.42 (s, 4H, 2CH<sub>2</sub>), 4.74 (s, 1H, CH), 7.39 (d,  $J = 8.7$  Hz, 2H, arom-H), 8.01 (d,

$J = 8.7$  Hz, 2H, arom-H); FT-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2959, 1662, 1515, 1470, 1361, 1344, 1201, 1166, 1139, 1002, 868.

*9-(4-Hydroxyphenyl)-3, 3, 6, 6-tetramethyl-1, 8-dioxo-octahydroxanthene (3f)*.  $^1\text{H}$  NMR ( $\delta$ , ppm): 1.02 (s, 6H, 2CH<sub>3</sub>), 1.12 (s, 6H, 2CH<sub>3</sub>), 2.16-2.31 (m, 4H, 2CH<sub>2</sub>), 2.48 (s, 4H, 2CH<sub>2</sub>), 4.69 (s, 1H, CH), 6.28 (s, 1H, OH), 6.58 (d,  $J = 8.4$  Hz, 2H, arom-H), 7.11 (d,  $J = 8.4$  Hz, 2H, arom-H); FT-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3411, 3023, 2962, 1663, 1614, 1596, 1513, 1449, 1425, 1360, 1200, 1166, 1107, 1003, 839.

*9-(4-Fluorophenyl)-3, 3, 6, 6-tetramethyl-1, 8-dioxo-octahydroxanthene (3g)*.  $^1\text{H}$  NMR ( $\delta$ , ppm): 1.02 (s, 6H, 2CH<sub>3</sub>), 1.13 (s, 6H, 2CH<sub>3</sub>), 2.15-2.32 (m, 4H, 2CH<sub>2</sub>), 2.49 (s, 4H, 2CH<sub>2</sub>), 4.75 (s, 1H, CH), 6.92 (t,  $J = 8.7$  Hz, 2H, arom-H), 7.25-7.32 (m, 2H, arom-H);  $^{13}\text{C}$  NMR ( $\delta$ , ppm): 27.3, 29.3, 31.2, 32.2, 40.9, 50.7, 114.7, 115.0, 115.5, 129.9, 139.9, 162.3, 196.4; FT-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2959, 1661, 1628, 1604, 1508, 1467, 1364, 1223, 1199, 1164, 1142, 1005, 851.

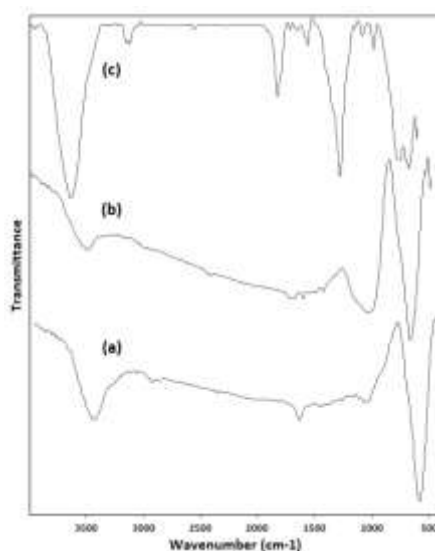
## Results and discussion

### Preparation and characterization of $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ MNPs

The preparation of a magnetically separable modified sulfuric acid ( $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ ) has been delineated through initial synthesis of  $\text{CuFe}_2\text{O}_4$  MNPs by a chemical coprecipitation of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in aqueous NaOH [50] followed by coating with a layer of silica using the sol-gel method by the ammonia-catalyzed hydrolysis of TEOS [51] and finally reaction with chlorosulfonic acid in *n*-hexane. The prepared  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  catalyst was characterized using FT-IR, SEM, EDX and VSM.

The FT-IR analysis of  $\text{CuFe}_2\text{O}_4$ ,  $\text{CuFe}_2\text{O}_4@\text{SiO}_2$  and  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  are shown in Figure 1. A strong band in the range of  $565\text{-}593\text{ cm}^{-1}$  appeared in the spectra of all MNPs (Figure 1, a-c) which can be assigned to the stretching vibration of Fe-O bond. The adsorption bands at  $3417\text{-}3445\text{ cm}^{-1}$  and also at  $1632\text{-}1648\text{ cm}^{-1}$  are assigned to OH groups and remaining  $\text{H}_2\text{O}$  in the samples. The additional peak in the range

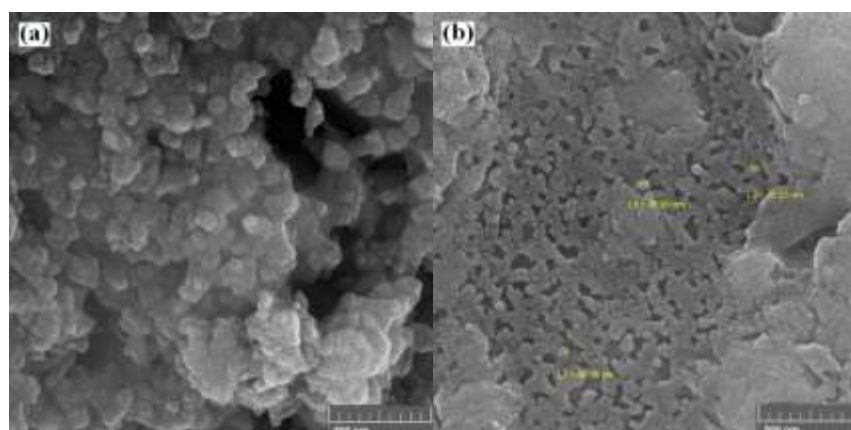
of  $955\text{-}1091\text{ cm}^{-1}$  recorded for MNPs having a  $\text{SiO}_2$  layer (Figure 1, b and c) was due to Si-O-Si antisymmetric stretching vibrations. Finally, the successful immobilization of  $\text{-SO}_3\text{H}$  group on the surface of  $\text{CuFe}_2\text{O}_4@\text{SiO}_2$  is confirmed by the appearance of the new characteristic peaks in the range of  $796\text{-}1370\text{ cm}^{-1}$  for the  $\text{SO}_2$  stretching vibrations (Figure 1c, overlapped with Si-O-Si).



**Figure 1.** FT-IR spectrum of (a)  $\text{CuFe}_2\text{O}_4$  (b)  $\text{CuFe}_2\text{O}_4@\text{SiO}_2$  and (c)  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$

To determine the morphology and size of the catalyst, SEM image of the  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  MNPs was prepared and compared to  $\text{CuFe}_2\text{O}_4$  MNPs (Figure 2). As shown in Figure 2(b), nanoparticles in the prepared

catalyst have spherical shape with an average diameter of approximately 40-50 nm, indicating that the nanocatalyst has a large surface area. The slight agglomeration is due to magnetic dipole interactions between the particles.

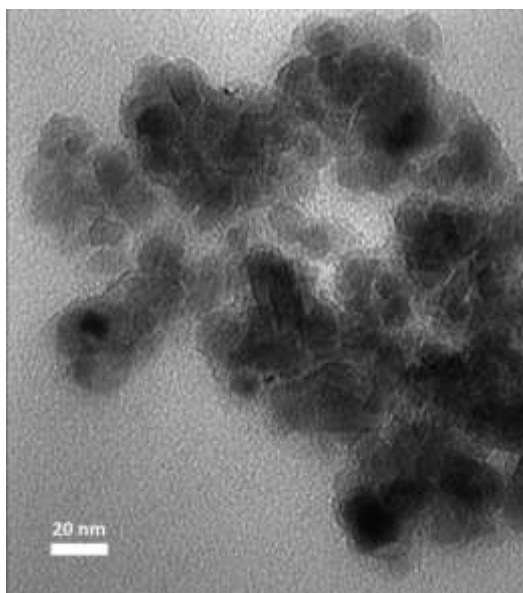


**Figure 2.** SEM images of (a)  $\text{CuFe}_2\text{O}_4$  and (b)  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  MNPs



Furthermore, the TEM image of the nanocatalyst shown in Figure 3 confirms the almost spherical shape of the

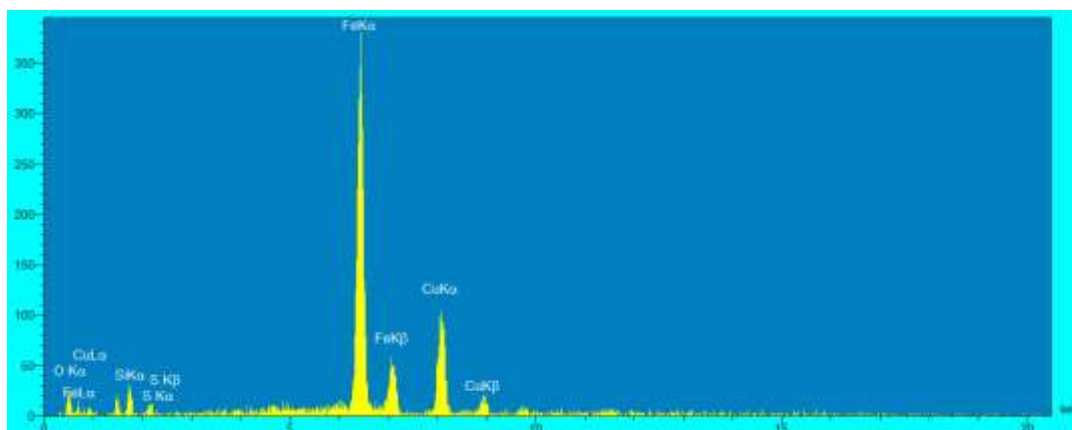
nanoparticles with diameters of less than 20 nm.



**Figure 3.** TEM image of  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  MNPs

The appearance of S along with other elements containing Cu, Fe, Si, and O in EDX spectrum of the  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  catalyst shows the successful immobilization of  $\text{SO}_3\text{H}$

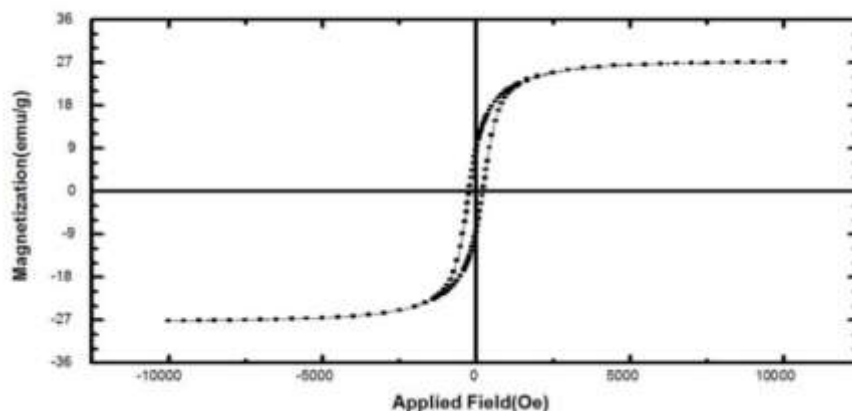
on  $\text{CuFe}_2\text{O}_4@\text{SiO}_2$  MNPs (Figure 4). As can be seen in Figure 4, no additional peak related to other impurities was appeared in the spectrum.



**Figure 4.** EDX analysis of  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  MNPs

Finally, the magnetic properties of  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  nanoparticles were studied using VSM at ambient temperature in an applied magnetic field, with the field sweeping from -10000 to +10,000 Oersted (Oe) (Figure 5). It could be seen that the hysteresis loop for the catalyst is relatively irreversible. This

confirms the ferromagnetic nature of the catalyst [52]. Furthermore, the saturation magnetization ( $M_s$ ) value of  $27.12 \text{ emu g}^{-1}$  shows that the catalyst has still sufficient magnetization for easy magnetic separation from a reaction mixture with a permanent magnet.



**Figure 5.** Hysteresis loop of  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  MNPs at room temperature

#### *Catalytic application of $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ MNPs*

The performance of  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  as an acidic nanocatalyst was tested in the synthesis of 1,8-dioxooctahydroxanthenes. In order to investigate the optimum amount of the catalyst, the effect of the solvent and influence of temperature, the reaction between dimedone **1** (1 mmol) and 4-chlorobenzaldehyde **2a** (1 mmol) for the synthesis of compound **3a** was selected as the test reaction. A summary of the optimization experiments is provided in Table 1. Because of the several advantages of solvent-free conditions in chemical reactions we firstly decided to investigate the model reaction under solvent-free conditions. As can be seen, the efficiency of the reaction is mainly affected by the amount of the  $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$  catalyst. No significant yield of the product was obtained in the absence of the catalyst

(Table 1, Entry 1) indicating that the catalyst is necessary for the reaction. Raising the amount of the catalyst increased the yield of the product **3a**. The best result was conducted in the presence of 0.04 g of the catalyst at 110 °C (Table 1, Entry 11). Higher amount of the catalyst and temperature did not improve the reaction time and yield of the product. Subsequently, the same model reaction in the presence of 0.04 g of catalyst was carried out in different solvents including  $\text{H}_2\text{O}$ , MeOH, EtOH,  $\text{CHCl}_3$  and  $\text{CH}_3\text{CN}$ , to assess the effect of solvent on the reaction. As shown, among the solvents tested and also solvent-free conditions, the yields of the reaction under solvent-free conditions were greater and the reaction times were generally shorter than the solvents. Therefore, all subsequent reactions were carried out using 0.04 g of the catalyst at 110 °C under solvent-free conditions.

**Table 1.** Optimization of reaction parameters for synthesis of compound **3a** catalyzed by CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-OSO<sub>3</sub>H MNPs<sup>a</sup>

Entry	Catalyst (g)	Solvent	T (°C)	Time (min)	Yield (%)
1	-----	-----	110	90	Trace
2	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.01)	-----	80	50	70
3	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.01)	-----	110	35	77
4	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.01)	-----	140	40	77
5	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.02)	-----	80	30	85
6	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.02)	-----	110	15	87
7	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.02)	-----	140	20	86
8	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.04)	-----	80	20	88
9	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.04)	-----	90	20	88
10	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.04)	-----	100	15	89
11	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.04)	-----	110	10	91
12	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.04)	-----	140	15	89
13	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.06)	-----	110	15	91
14	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.04)	H <sub>2</sub> O	Reflux	30	76
15	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.04)	MeOH	Reflux	50	79
16	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.04)	EtOH	Reflux	40	81
17	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.04)	CHCl <sub>3</sub>	Reflux	60	70
18	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H MNPs (0.04)	CH <sub>3</sub> CN	Reflux	50	72
19	CuFe <sub>2</sub> O <sub>4</sub> MNPs (0.04)	-----	110	40	36
20	CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> MNPs (0.04)	-----	110	40	22

<sup>a</sup>Reaction conditions: dimedone **1** (2 mmol), 4-chlorobenzaldehyde **2a** (1 mmol).

Next, in order to evaluate the generality of this model reaction, the catalytic activity of the catalyst was tested using different aromatic aldehydes in the reaction with dimeone under optimized reaction conditions. As shown in Table 2, all the reactions on a wide

range of aromatic aldehydes bearing both electron-donating (methyl, hydroxyl and methoxy) and electron-withdrawing (halogens and nitro) substituents afforded excellent yields of the corresponding product **3a-j**.



**Table 2.** Synthesis of 1,8-dioxo-octahydroxanthenes **3a-j** using CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-OSO<sub>3</sub>H MNPs<sup>a</sup>

Entry	R	Product	Time (min)	Isolated Yield (%)	mp (°C)	
					Find	Reported
<b>1</b>	4-Cl	<b>3a</b>	10	91	233-235	230-233 [17]
<b>2</b>	2-Cl	<b>3b</b>	10	94	228-230	230-232 [17]
<b>3</b>	4-Br	<b>3c</b>	8	91	235-237	232-233 [16]
<b>4</b>	4-NO <sub>2</sub>	<b>3d</b>	8	93	225-227	227-228 [16]
<b>5</b>	3-NO <sub>2</sub>	<b>3e</b>	12	94	176-178	171-173 [17]
<b>6</b>	4-OH	<b>3f</b>	12	90	250-253	247-249 [16]
<b>7</b>	4-F	<b>3g</b>	10	93	229-231	225-227 [16]
<b>8</b>	4-Me	<b>3h</b>	10	95	214-215	212-214 [17]
<b>9</b>	4-MeO	<b>3i</b>	12	92	241-243	244-246 [48]
<b>10</b>	H	<b>3j</b>	12	92	197-199	200-202 [48]

<sup>a</sup>Reaction conditions: dimedone **1** (2 mmol), an aromatic aldehyde **2a-j** (1 mmol), CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-OSO<sub>3</sub>H MNPs (0.04 g), 110 °C, solvent-free.

The obtained results using CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-OSO<sub>3</sub>H as a heterogeneous catalyst were compared with those using other catalysts reported for the synthesis of 1,8-dioxo-octahydroxanthenes. This comparison is

shown in Table 3. As can be seen, our reaction conditions showed a shorter reaction time than the other conditions and gave high yields of the desired products

**Table 3.** Comparison of the efficiencies of different catalysts for the synthesis of 1,8-dioxo-octahydroxanthenes

Catalyst	Conditions			Time (min)	Yield (%)	Ref.
	Solvent	T (°C)	Other			
Sulfated zirconia	EtOH	70	-----	480	84-95	[10]
MWCNT-BuSO <sub>3</sub> H	EtOH	r.t.	-----	25-40	91-96	[11]
β-CD-BSA	H <sub>2</sub> O	reflux	-----	15-60	88-97	[12]
CAN/HY-zeolite	-----	80	-----	45-160	72-93	[13]
Silica/Preyssler NPs	H <sub>2</sub> O	reflux	-----	180	82-96	[14]
L-Proline	ClCH <sub>2</sub> CH <sub>2</sub> Cl	60	-----	360	59-90	[15]
ZnO nanoparticles	EtOH	reflux	-----	30-150	78-98	[16]
SmCl <sub>3</sub>	-----	120	-----	480-1440	20-98	[17]
Nanosized MCM-41-SO <sub>3</sub> H	H <sub>2</sub> O	60	Ultrasound	15-90	86-99	[18]
Trimethylsilyl chloride	CH <sub>3</sub> CN	reflux	-----	480-600	72-84	[19]
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /MCM-41	EtOH	reflux	-----	300	74-94	[20]
[Et <sub>3</sub> NC <sub>4</sub> SO <sub>3</sub> H]/[HSO <sub>4</sub> ]/Al <sub>2</sub> O <sub>3</sub>	-----	120	-----	30-40	78-97	[21]
CuFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> -OSO <sub>3</sub> H	-----	110	-----	8-12	90-95	This work

The reusability of the catalyst was also investigated. For this purpose, the same model reaction was again studied under optimized conditions. After the completion of the reaction, hot acetone was added to the reaction mixture to dissolve the product. With the aid of an external magnet, the catalyst was held on the sidewall of the reaction vessel, while the solution was decanted. The catalyst was washed with acetone and ethanol, dried at 100 °C under vacuum for 1 h, and reused for a similar reaction. The catalyst could be used at least four times with only a slight reduction in activity (91, 90, 88, and 87% yields for first to fourth use, respectively) which clearly demonstrates the practical reusability of this catalyst.

### Conclusion

In summary, we report a new, simple and green catalytic method for the synthesis of 1,8-dioxo-octahydroxanthenes *via* the reaction of aromatic aldehydes with dimedone using sulfuric acid linked on silica-coated CuFe<sub>2</sub>O<sub>4</sub> MNPs (CuFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H) at 110 °C under solvent-free conditions. The catalyst could simply be recovered with the aid of an external magnet, and used at least four times without significant loss of its catalytic activity. High yields, short reaction times, easy work-up, and the absence of any volatile and hazardous organic solvents are some advantages of this protocol.

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### References

- [1] S. Naseem, M. Khalid, M.N. Tahir, M.A. Halim, A.A.C. Braga, M.M. Naseer, Z. Shafiq, *J. Mol. Struct.*, **2017**, *1143*, 235-244.
- [2] K. Reddi Mohan Naidu, B. Satheesh Krishna, M. Anil Kumar, P. Arulselvan, S. Ibrahim Khalivulla, O. Lasekan, *Molecules*, **2012**, *17*, 7543-7555.
- [3] H. Hafez, M. Hegab, I. Ahmed-Farag, A. El-Gazzar, *Bioorg. Med. Chem. Lett.*, **2008**, *18*, 4538-4543.
- [4] H. Wang, L. Lu, S. Zhu, Y. Li, W. Cai, *Curr. Microbiol.*, **2006**, *52*, 1-5.
- [5] C. Spatafora, V. Barresi, V.M. Bhusainahalli, S. Di Micco, N. Musso, R. Riccio, G. Bifulco, D. Condorelli, C. Tringali, *Org. Biomol. Chem.*, **2014**, *12*, 2686-2701.
- [6] Y. Song, Y. Yang, J. You, B. Liu, L. Wu, Y. Hou, W. Wang, J. Zhu, *Chem. Pharm. Bull.*, **2013**, *61*, 167-175.
- [7] K. Razmkhah, H. Little, S. Sandhu, T.R. Dafforn, A. Rodger, *RSC Adv.*, **2014**, *4*, 37510-37515.
- [8] L. Cerdán, V. Martínez-Martínez, I. García-Moreno, A. Costela, M.E. Pérez-Ojeda, I.L. Arbeloa, L. Wu, K. Burgess, *Adv. Opt. Mater.*, **2013**, *1*, 984-990.
- [9] N. Sekar, *Colourage* **2003**, *50*, 59-60.
- [10] S.S. Kahandal, A.S. Burange, S.R. Kale, P. Prinsen, R. Luque, R.V. Jayaram, *Catal. Commun.*, **2017**, *97*, 138-145.
- [11] K.P. Boroujeni, Z. Heidari, R.Khalifeh, *Acta Chim. Slov.*, **2016**, *63*, 602-608.
- [12] K. Gong, H. Wang, S. Wang, Y. Wang, J. Chen, *Chin. J. Catal.*, **2015**, *36*, 1249-1255.
- [13] P. Sivaguru, A. Lalitha, *Chin. Chem. Lett.*, **2014**, *25*, 321-323.
- [14] A. Javid, M.M. Heravi, F.F. Bamoharram, *J. Chem.*, **2011**, *8*, 910-916.
- [15] B. Das, J. Kashanna, R.A. Kumar, P. Jangili, *Synth. Commun.*, **2012**, *42*, 2876-2884.
- [16] Z. Lasemi, E. Mehrasbi, *Res. Chem. Intermed.*, **2015**, *41*, 2855-2866.
- [17] A. Ilangovan, S. Malayappasamy, S. Muralidharan, S.

- Maruthamuthu, *Chem. Cent. J.*, **2011**, *5*, Art. No. 81, 1-6.
- [18] S. Rostamizadeh, A.M. Amani, G.H. Mahdavinia, G. Amiri, H. Sepehrian, *Ultrason. Sonochem.*, **2010**, *17*, 306-309.
- [19] S. Kantevari, R. Bantu, L. Nagarapu, *Arkivoc*, **2006**, *16*, 136-148.
- [20] G. Karthikeyan, A. Pandurangan, *J. Mol. Catal. A: Chem.*, **2009**, *311*, 36-45.
- [21] M. Khoshnevis, A. Davoodnia, A. Zare-Bidaki, N. Tavakoli-Hoseini, *Synth. React. Inorg. Metal-Org. Nano-Met. Chem.*, **2013**, *43*, 1154-1161.
- [22] A. Fihri, C. Len, R.S. Varma, A. Solhy, *Coord. Chem. Rev.*, **2017**, *347*, 48-76.
- [23] L. Youseftabar-Miri, *Iran. Chem. Commun.*, **2019**, *7*, 142-152.
- [24] N. Nami, M. Tajbakhsh, M. Vafakhah, *Iran. Chem. Commun.*, **2019**, *7*, 93-101.
- [25] M. Rohaniyan, A. Davoodnia, A. Nakhaei, *Appl. Organomet. Chem.*, **2016**, *30*, 626-629.
- [26] A. Davoodnia, M.M. Heravi, R. Rezaei-Daghigh, T. Tavakoli-Hoseini, *Chin. Chem. Lett.*, **2010**, *28*, 429-433.
- [27] S.C. Azimi, K. Rad-Moghadam, *Iran. Chem. Commun.*, **2015**, *3*, 356-366.
- [28] M. Hara, *ChemSusChem*, **2009**, *2*, 129-135.
- [29] H. Salavati, A. Teimouri, S. Kazemi, *Chem. Methodol.*, **2017**, *1*, 12-27.
- [30] D. Wang, D. Astruc, *Chem. Rev.*, **2014**, *114*, 6949-6985.
- [31] L. Wu, A. Mendoza-Garcia, Q. Li, S. Sun, *Chem. Rev.*, **2016**, *116*, 10473-10512.
- [32] E. Teymooria, A. Davoodnia, A. Khojastehnezhad, N. Hosseininasab, *Iran. Chem. Commun.*, **2019**, *7*, 271-282
- [33] A. Khorshidi, S. Shariati, M. Aboutalebi, N. Mardazad, *Iran. Chem. Commun.*, **2016**, *4*, 476-482.
- [34] H. Saeidian, H. Sadighian, M. Arabgari, Z. Mirjafary, S.E. Ayati, E. Najafi, F. Matloubi Moghaddam, *Res. Chem. Intermed.*, **2018**, *44*, 601-612.
- [35] Z. Arzehgar, A. Aydi, M. Mirzaei Heydari, *Asian J. Green Chem.*, **2018**, *2*, 281-298.
- [36] N. Rasouli, M. Movahedi, E.A. Naeini, *Iran. Chem. Commun.*, **2018**, *6*, 169-179.
- [37] F. Matloubi Moghaddama, M. Doulabi, H. Saeidian, *Sci. Iran. C*, **2012**, *19*, 1597-1600.
- [38] M.A. Zolfigol, F. Karimi, M. Yarie, M. Torabi, *Appl. Organometal. Chem.*, **2018**, *32*, Art. No. e4063.
- [39] E. Rezaee Nezhad, R. Tahmasebi, *Asian J. Green Chem.*, **2019**, *3*, 34-42.
- [40] M. Khodajoo, S. Sayyahi, S.J. Saghanezhad, *Russ. J. Gen. Chem.*, **2016**, *86*, 1177-1181.
- [41] A. Emrani, A. Davoodnia, N. Tavakoli-Hoseini, *Bull. Korean Chem. Soc.*, **2011**, *32*, 2385-2390.
- [42] G. Yassaghi, A. Davoodnia, S. Allameh, A. Zare-Bidaki, N. Tavakoli-Hoseini, *Bull. Korean Chem. Soc.*, **2012**, *33*, 2724-2730.
- [43] A. Davoodnia, M. Khashi, N. Tavakoli-Hoseini, *Chin. J. Catal.*, **2013**, *34*, 1173-1178.
- [44] M. Khashi, A. Davoodnia, V.S. Prasada Rao Lingam, *Res. Chem. Intermed.*, **2015**, *41*, 5731-5742.
- [45] A. Davoodnia, A. Nakhaei, N. Tavakoli-Hoseini, *Z. Naturforsch.*, **2016**, *71b*, 219-225.
- [46] S. Ameli, A. Davoodnia, M. Pordel, *Org. Prep. Proced. Int.*, **2016**, *48*, 328-336.
- [47] M. Fattahi, A. Davoodnia, M. Pordel, *Russ. J. Gen. Chem.*, **2017**, *87*, 863-867.
- [48] F. Tajfirooz, A. Davoodnia, M. Pordel, M. Ebrahimi, A.

Khojastehnezhad, *Appl. Organometal. Chem.*, **2018**, 32, Art. No. e3930.

[49] N. Hosseininasab, A. Davoodnia, F. Rostami-Charati, A. Khojastehnezhad, *Russ. J. Gen. Chem.*, **2017**, 87, 2436-2443.

[50] A. Bazgir, G. Hosseini, R. Ghahremanzadeh, *ACS Comb. Sci.*, **2013**, 15, 530-534.

[51] S. Swami, A. Agarwala, R. Shrivastava, *New J. Chem.*, **2016**, 40, 9788-9794.

[52] D.C. Jiles, D.L. Atherton, *J. Magn. Magn. Mater.*, **1986**, 61, 48-60.

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