

Scientific paper

# Carbon Nanotube-Supported Butyl 1-Sulfonic Acid Groups as a Novel and Environmentally Compatible Catalyst for the Synthesis of 1,8-Dioxo-octahydroxanthenes

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## Abstract

A novel multiwalled carbon nanotube catalyst with  $-\text{SO}_3\text{H}$  functional groups was easily prepared from its starting materials and used as an efficient heterogeneous catalyst for one-pot Knoevenagel condensation, Michael addition, and cyclodehydration of 5,5-dimethyl-1,3-cyclohexanedione (dimedone) with various aromatic aldehydes. Using this method 1,8-dioxo-octahydroxanthenes were obtained in excellent yields at room temperature. The present method is superior in terms of reaction temperature, reaction time, easy work-up, high yields, and ease of recovery of catalyst.

**Keywords:** Nanocatalyst; Heterogeneous catalysis; 1,8-Dioxo-octahydroxanthene; Aldehyde; 5,5-Dimethyl-1,3-cyclohexanedione

## 1. Introduction

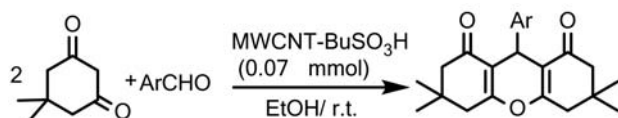
Recently, carbon nanotubes (CNTs) have been considered as good supports for homogeneous and heterogeneous catalysts.<sup>1–3</sup> When compared to other commonly used supports in heterogeneous catalysis, CNTs present the advantage of extraordinary electrical, thermal, and mechanical strength characteristics, resistance to chemical attack in acidic and basic media, high surface areas, and low cost. They are cylindrically shaped and their surface can be modified with various functional groups, which can be used as building blocks for covalent and noncovalent attachment of catalytic active species.

There is a widespread interest in the synthesis of xanthene derivatives owing to their diverse range of biological and therapeutic properties, such as anti-inflammatory,<sup>4</sup> antiviral,<sup>5</sup> and anticancer activities.<sup>6</sup> Also, they were used as antagonists for the paralyzing action of zoxazolamine,<sup>7</sup> fluorescent markers for the visualization of biomolecules,<sup>8</sup> and photostable laser dyes.<sup>9</sup> Among various derivatives of xanthene, 1,8-dioxo-octahydroxanthenes have aroused considerable interest. Synthesis of 1,8-dioxo-octahydroxanthenes is generally achieved by the con-

densation of dimedone with aldehydes. Several types of catalysts were introduced previously for this reaction, such as  $\text{NaHSO}_4\text{-SiO}_2$  or silica chloride,<sup>10</sup> polyphosphoric acid- $\text{SiO}_2$ ,<sup>11</sup>  $\text{In}(\text{OTf})_3$ ,<sup>12</sup>  $\text{H}_2\text{SO}_4$ ,<sup>13</sup>  $\text{InCl}_3$  or  $\text{P}_2\text{O}_5$ ,<sup>14</sup> ceric ammonium nitrate (CAN) under ultrasound irradiation,<sup>15</sup> succinimide-*N*-sulfonic acid,<sup>16</sup>  $\text{CaCl}_2$ ,<sup>17</sup>  $\text{Fe}_3\text{O}_4$  nanoparticles,<sup>18</sup> CAN supported HY-zeolite,<sup>19</sup>  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ -Imid- $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  nanoparticles,<sup>20</sup> piperidine,<sup>21</sup> Mg-Al hydroxalite,<sup>22</sup> thiourea dioxide,<sup>23</sup> and ZnO nanoparticles.<sup>24</sup> Although these methods are suitable for certain synthetic conditions, there exist some drawbacks, such as low yields, high reaction temperature, long reaction times, tedious work-up, the formation of 2,2'-aryl-methylene bis(3-hydroxy-2-cyclohexene-1-one) derivatives due to competitive side reactions, and the use of unrecyclable, hazardous or difficult to handle catalysts. In view of this, utilizing eco-friendly and green catalysts for this useful reaction is in demand.

In a continuation of our recent work on synthesis and application of heterogeneous catalysts in organic reactions,<sup>25–28</sup> herein we now report the synthesis of multiwalled carbon nanotube-supported butyl 1-sulfonic acid groups (MWCNT-BuSO<sub>3</sub>H) from the reaction of the salt

form hydroxyl functionalized multiwalled carbon nanotube (MWCNT–OH) with 1,4-butane sultone followed by the reaction with HCl. MWCNT–BuSO<sub>3</sub>H was used as a heterogeneous catalyst for one-pot Knoevenagel condensation, Michael addition, and cyclodehydration of dimedone with various aromatic aldehydes at room temperature (Scheme 1).



**Scheme 1.** Synthesis of 1,8-dioxo-octahydroxanthenes using MWCNT–BuSO<sub>3</sub>H.

## 2. Experimental

### 2. 1. Materials and Methods

Chemicals were either prepared in our laboratory or were purchased from Merck and Fluka. Reaction monitoring and purity determination of the products were accomplished by GLC or TLC on silica-gel polygram SILG/UV<sub>254</sub> plates. Gas chromatography was recorded on Shimadzu GC 14-A. IR spectra were obtained by a Shimadzu model 8300 FT-IR spectrophotometer. <sup>1</sup>H NMR spectra were recorded on 400 MHz spectrometer in CDCl<sub>3</sub>. The Leco sulfur analyzer was used for the measurement of sulfur in the catalyst. TGA was carried out on a Stanton Redcraft STA-780 with a 20 °C/min heating rate. SEM and TEM images were taken with a Hitachi S-3400N scanning electron microscope and a Philips CM10 transmission electron microscope, respectively. Melting points were determined on a Fisher–Jones melting-point apparatus.

### 2. 2. Synthesis of Multiwalled Carbon Nanotubes

MWCNT and MWCNT–OH were prepared as reported in our previous work.<sup>1</sup>

### 2. 3. Synthesis of MWCNT–BuSO<sub>3</sub>H

In a round bottomed flask (50 mL) equipped with a reflux condenser was added 1 g of the MWCNT–OH to an aqueous solution of sodium hydroxide (1 M, 10 mL) and the mixture was stirred at 60 °C for 12 h, filtered, washed with distilled water (20 mL), and dried at 80 °C overnight to give MWCNT–ONa. Then, 1,4-butane sultone (1.5 mL) was added to the obtained solid and the mixture was stirred at 100 °C for 24 h, filtered, washed with distilled water (20 mL), and dried at 80 °C overnight to give MWCNT–OBuSO<sub>3</sub>Na. Afterwards, HCl (3 M, 10 mL) was added to MWCNT–OBuSO<sub>3</sub>Na and the mixture was stirred at room temperature for 2 h, filtered, washed with distilled

water (20 mL), and dried at 80 °C overnight to give MWCNT–BuSO<sub>3</sub>H.

### 2. 4. General Procedure for 1,8-Dioxo-octahydroxanthene Synthesis

A mixture of an aldehyde (2 mmol), dimedone (0.28 g, 2 mmol), MWCNT–BuSO<sub>3</sub>H (0.066 g, 0.07 mmol), and ethanol (3 mL) was stirred for an appropriate time at room temperature. After completion of the reaction (monitored by TLC), the catalyst was filtered off and washed with ethanol (2 × 10 mL). Then, the filtrate was concentrated on a rotary evaporator under reduced pressure and the crude product recrystallized from ethanol. All products are known compounds and were identified by comparison of their physical and spectral data with those of the authentic samples.

### 2. 5. Representative Spectral Data of Some of the Obtained Compounds

**3,3,6,6-Tetramethyl-9-phenyl-1,8-dioxo-octahydroxanthene**<sup>14</sup> (Table 1, entry 1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.01 (s, 6H, 2 CH<sub>3</sub>), 1.14 (s, 6H, 2 CH<sub>3</sub>), 2.19–2.48 (m, 8H, 4 CH<sub>2</sub>), 4.80 (s, 1H, CH), 6.95–7.22 (m, 5H, ArH). IR (KBr) ν 2960, 2950, 1663, 1490, 1390, 1250, 850 cm<sup>-1</sup>.

**9-(4'-Nitrophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione**<sup>14</sup> (Table 1, entry 11). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.05 (s, 6H, 2 CH<sub>3</sub>), 1.16 (s, 6H, 2 CH<sub>3</sub>), 2.20–2.50 (m, 8H, 4 CH<sub>2</sub>), 4.88 (s, 1H, CH), 7.52–7.60 (d, 2H, ArH), 8.09–8.14 (d, 2H, ArH). IR (KBr) ν 2966, 2930, 2870, 1730, 1670, 1600, 1350, 1192, 860 cm<sup>-1</sup>.

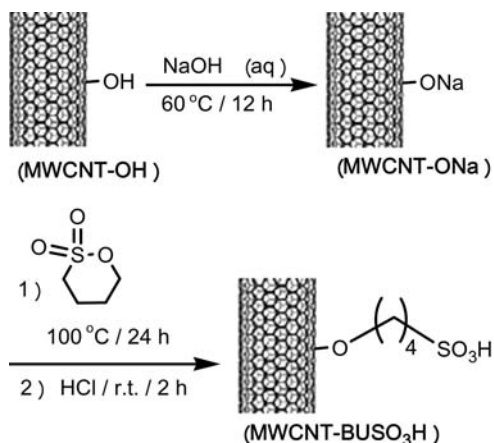
**9-(4-Methoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione**<sup>12</sup> (Table 1, entry 4). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.06 (s, 6H, 2 CH<sub>3</sub>), 1.14 (s, 6H, 2 CH<sub>3</sub>), 2.19–2.48 (m, 8H, 4 CH<sub>2</sub>), 3.80 (s, 3H, OCH<sub>3</sub>), 4.72 (s, 1H, CH), 6.83–6.91 (d, 2H, ArH), 7.20–7.23 (d, 2H, ArH). IR (KBr) ν 2960, 2948, 1668, 1200, 1190, 795 cm<sup>-1</sup>.

## 3. Results and Discussion

### 3. 1. Preparation of MWCNT–BuSO<sub>3</sub>H

A chemical vapour deposition (CVD) method was used for the synthesis of MWCNT.<sup>1</sup> In order to develop hydroxyl groups on the MWCNT surface, the carbon nanomaterials were submitted to a heat treatment in a synthetic air flow (10 mL/min) at 500 °C for 2 h.<sup>1</sup>

The synthetic routes for the MWCNT–BuSO<sub>3</sub>H are shown in Scheme 2. At the first stage, MWCNT–OH was treated with NaOH to form the MWCNT–ONa. In the second step, MWCNT–BuSO<sub>3</sub>H was prepared from the reac-



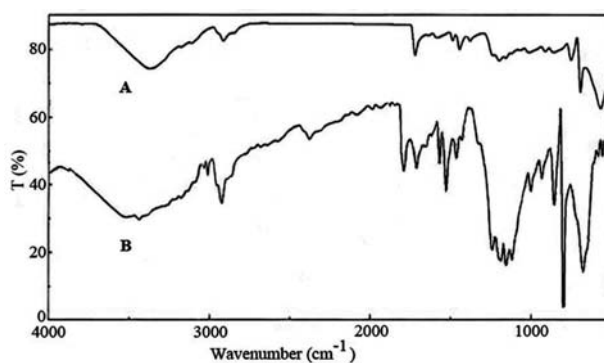
**Scheme 2.** Preparation procedure to MWCNT-BuSO<sub>3</sub>H.

tion of MWCNT-ONa with 1,4-butane sultone followed by the reaction with HCl. The resulting black solid was analyzed by elemental analysis to quantify the percentage loading of the sulfonic acid groups by measuring the sulfur content, giving 0.98 mmol sulfonic acid moiety per gram. The acidic sites loading in MWCNT-BuSO<sub>3</sub>H obtained by means of acid-base titration was found to be 1.05 mmol/g.<sup>25</sup>

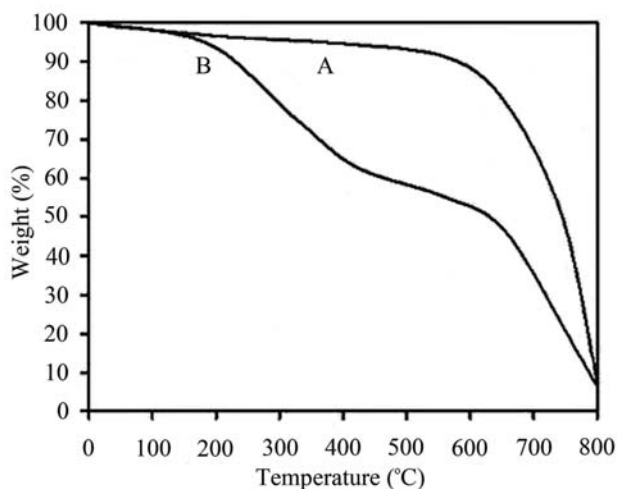
### 3. 2. Characterization of MWCNT-BuSO<sub>3</sub>H

FT-IR spectra of the MWCNT-OH and MWCNT-BuSO<sub>3</sub>H are presented in Figure 1. As can be seen in the spectrum of MWCNT-BuSO<sub>3</sub>H new peaks appeared at 1120, 1150, 1190, and 1230 cm<sup>-1</sup>, which can be assigned to S=O stretching vibration.<sup>25,26</sup>

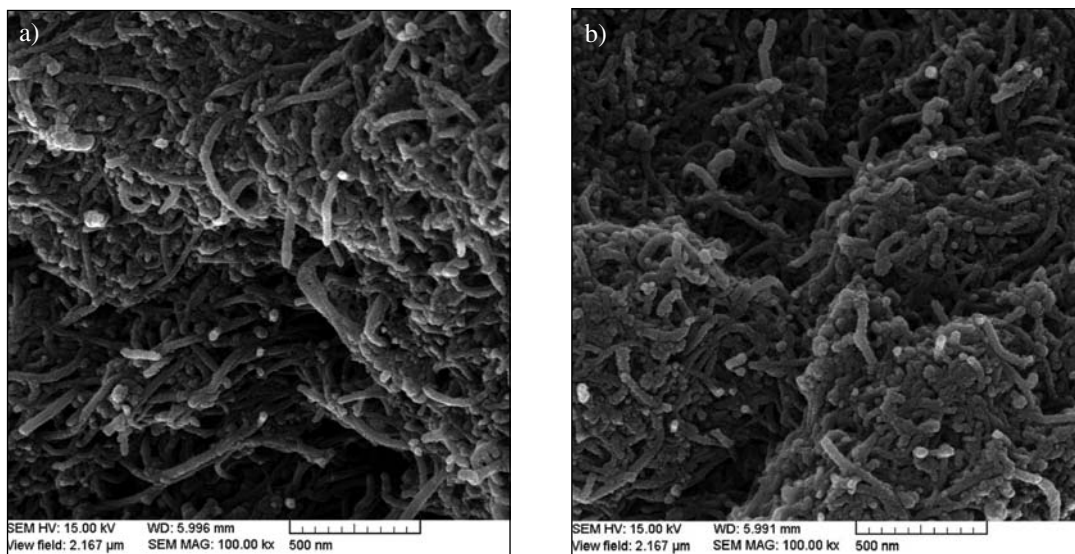
The thermogravimetric analyses (TGA) of MWCNTs, before and after the functionalization processes, are provided in Figure 2. The TGA curves of MWCNT-OH and



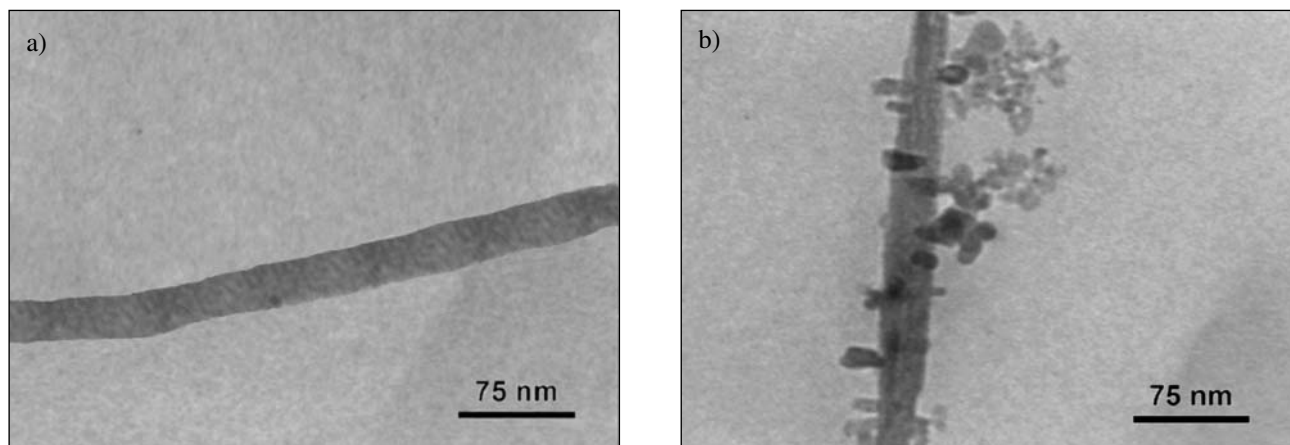
**Figure 1.** FT-IR spectra of MWCNT-OH (A) and MWCNT-BuSO<sub>3</sub>H (B).



**Figure 2.** TGA curves of MWCNT-OH (A) and MWCNT-BuSO<sub>3</sub>H (B).



**Figure 3.** SEM photographs of MWCNT-OH (a) and MWCNT-BuSO<sub>3</sub>H (b).



**Figure 4.** TEM photographs of MWCNT–OH (a) and MWCNT–BuSO<sub>3</sub>H (b).

MWCNT–BuSO<sub>3</sub>H displayed a weight loss around 100 °C which is corresponding to the loss of the physically adsorbed water. In the case of MWCNT–BuSO<sub>3</sub>H, the second weight loss started at about 180 °C and is mainly assigned to the decomposition of the alky-sulfonic acid groups. In TGA curves of MWCNT–OH and MWCNT–BuSO<sub>3</sub>H the last weight losses at about 570–640 °C were likely due to the degradation of MWCNTs.

An attempt was made to investigate the morphology of the MWCNTs using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). From SEM photographs of MWCNT–OH and MWCNT–BuSO<sub>3</sub>H (Figure 3), it is obvious that the MWCNTs are well distributed and no amorphous carbon is detected. In the TEM photograph of MWCNT–BuSO<sub>3</sub>H (Figure 4 (B)), it can be seen that the CNTs do not suffer damage after the functionalization and anion-exchange processes and that there are small particles affixed on the surface of MWCNT due to functionalization processes.

### 3. 3. Catalytic Activity of MWCNT–BuSO<sub>3</sub>H

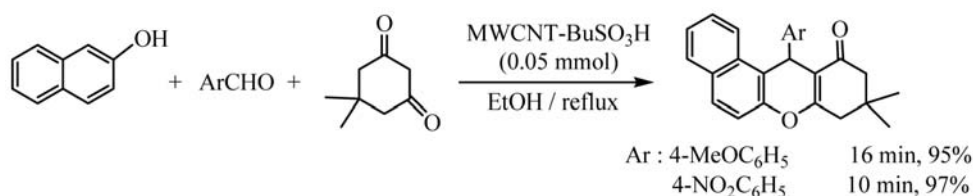
In order to explore the catalytic activity of MWCNT–BuSO<sub>3</sub>H, we studied the synthesis of 1,8-dioxo-octahydroxanthenes by the reaction of aldehydes with dimedone. Initially, to optimize the reaction conditions, we tried to convert benzaldehyde to 3,3,6,6-tetramethyl-9-phenyl-1,8-dioxo-octahydroxanthene with dimedone at different conditions and various molar ratios of substrates. The best results were obtained at room temperature and a molar ratio of benzaldehyde:dimedone:MWCNT–BuSO<sub>3</sub>H of 1:2:0.07. Then, under optimal conditions, a wide variety of substituted benzaldehydes (containing both electron withdrawing and donating groups) and 1-naphthaldehyde were treated with dimedone to give the corresponding products in high to excellent yields (Table 1, entries 1–13). Acid sensitive substrates, such as thiophene-2-carbaldehyde and cinnamaldehyde gave the cor-

responding products without generation of polymeric by-products under the present reaction conditions (entries 14,15). In the case of substituted benzaldehydes, the 2-substituted isomer (entries 8,9,12) was less reactive than the 4-substituted isomer, probably due to the increased steric hindrance. It is noteworthy that no competitive side reactions such as the formation of 2,2'-aryl-methylene bis(3-hydroxy-2-cyclohexene-1-one) derivatives were observed in these transformations.<sup>10,17</sup>

To the best of our knowledge synthesis of 1,8-dioxo-octahydroxanthenes from the reaction of aldehydes with dimedone at room temperature is rare. Most of the reported methods need high temperatures or the use of an additional energy (ultrasound or microwave).<sup>29,30</sup>

Following these results, we further investigated the potential of MWCNT–BuSO<sub>3</sub>H for the synthesis of tetrahydrobenzo[*a*]xanthen-11-ones through condensation of aldehydes, dimedone, and 2-naphthol at room temperature with ethanol as the solvent. We observed that tetrahydrobenzo[*a*]xanthen-11-ones were obtained in moderate yields after long reaction times. However, when the reactions were carried out in refluxing ethanol the desired products were obtained in high yields at very short reaction times in the presence of 0.05 mmol of catalyst (Scheme 3). In comparison with the other catalysts employed for the synthesis of tetrahydrobenzo[*a*]xanthen-11-ones,<sup>31,32</sup> MWCNT–BuSO<sub>3</sub>H showed a higher catalytic activity in terms of shorter reaction time and higher yields.

As shown in Table 1 (entries 10,11), the aromatic aldehydes with electron withdrawing groups reacted very well at faster rate compared with aromatic aldehydes substituted with electron releasing groups. This observation can be rationalized on the basis the mechanistic details of the reaction (Scheme 4). The aldehyde is first activated by MWCNT–BuSO<sub>3</sub>H. Nucleophilic addition of dimedone to the activated aldehyde followed by the loss of H<sub>2</sub>O generates intermediate I, which is further activated by MW-



**Scheme 3.** Synthesis of tetrahydrobenzo[*a*]xanthen-11-ones using MWCNT–BuSO<sub>3</sub>H.

CNT–BuSO<sub>3</sub>H. Then, the 1,4-nucleophilic addition of a second molecule of dione on the activated intermediate I, in the Michael addition fashion, affords the intermediate II, which undergoes intramolecular cyclodehydration to give the 1,8-dioxo-octahydroxanthene. The electron withdrawing groups present on the aromatic al-

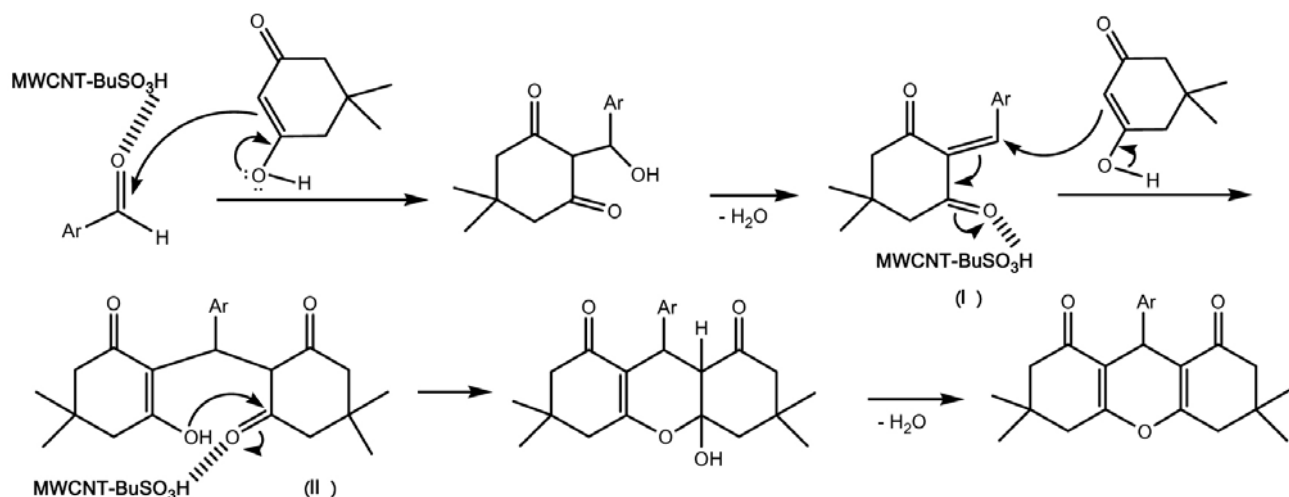
dehyde in the intermediate I increase the rate of 1,4-nucleophilic addition reaction because the alkene LUMO is at lower energy in their presence compared with the aldehydes possessing electron donating groups.<sup>33</sup>

The reusability of the MWCNT–BuSO<sub>3</sub>H was also determined. MWCNT–BuSO<sub>3</sub>H recovered after the reac-

**Table 1:** Synthesis of 1,8-dioxo-octahydroxanthenes.

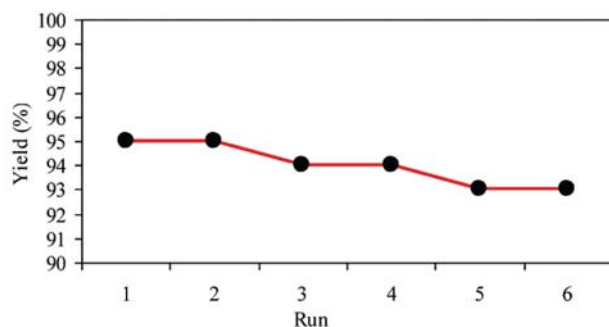
Entry	Aldehyde	Time (min)	Yield (%) <sup>a,b</sup>	mp (°C) (lit.) <sup>ref.</sup>
1	Benzaldehyde	30	95	201–203 (204–205) <sup>14</sup>
2	4-Methylbenzaldehyde	35	94	210–215 (213–215) <sup>14</sup>
3	4-Isopropylbenzaldehyde	36	95	201–203 (203–206) <sup>18</sup>
4	4-Methoxybenzaldehyde	37	96	240–243 (242–244) <sup>12</sup>
5	3-Methoxybenzaldehyde	36	93	163–165 (162–165) <sup>11</sup>
6	4-Hydroxybenzaldehyde	40	93	243–245(249–251) <sup>14</sup>
7	4-Chlorobenzaldehyde	30	95	228–231 (231–233) <sup>20</sup>
8	2-Chlorobenzaldehyde	35	91	226–228 (224–226) <sup>23</sup>
9	2,4-Dichlorobenzaldehyde	35	92	249–253 (248–250) <sup>11</sup>
10	4-Cyanobenzaldehyde	26	95	222–225 (218–220) <sup>23</sup>
11	4-Nitrobenzaldehyde	25	96	225–227 (223–224) <sup>14</sup>
12	2-Nitrobenzaldehyde	28	91	260–263 (259–261) <sup>12</sup>
13	1-Naphthaldehyde	40	95	235–237 (232–234) <sup>12</sup>
14	Thiophene-2-carbaldehyde	35	94	162–164 (161–162) <sup>14</sup>
15	Cinnamaldehyde	36	93	179–181 (177–178) <sup>22</sup>

<sup>a</sup> Isolated yield, <sup>b</sup> All products are known compounds and were identified by comparison of their melting points and <sup>1</sup>H NMR and FT-IR data with those of the authentic samples.



**Scheme 4.** Suggested mechanism for the preparation of 1,8-dioxo-octahydroxanthenes.

tion can be washed with EtOH and used again at least six times without any noticeable loss of catalytic activity (Figure 5).



**Figure 5.** Recyclability of MWCNT–BuSO<sub>3</sub>H (0.07 mmol) in the reaction of benzaldehyde (1 mmol) with dimedone (2 mmol) at room temperature. Reaction time 30 min.

To show the merit of the present work in comparison with the other results reported in the literature, we compared results of MWCNT–BuSO<sub>3</sub>H with selected previously known protocols in the synthesis of 1,8-dioxo-octahydroxanthenes (Table 2). As can be seen in addition to having the general advantages attributed to the solid catalysts, MWCNT–BuSO<sub>3</sub>H has a good efficiency compared to many of other reported catalysts in the synthesis of 1,8-dioxo-octahydroxanthenes.

## 4. Conclusion

In conclusion, we synthesized a novel multiwalled carbon nanotube catalyst with –SO<sub>3</sub>H functional groups.

This reusable heterogeneous acid catalyst preserved high catalytic activity for the synthesis of 1,8-dioxo-octahydroxanthenes. Easy preparation and handling of the catalyst, easy workup, high selectivity, excellent yields, short reaction times, and mild reaction conditions are the obvious advantages of the present method.

## 5. Acknowledgement

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**Table 2:** Comparison of the efficiencies of a number of different reported catalysts with that of MWCNT–BuSO<sub>3</sub>H in the reaction of benzaldehyde with dimedone.

Entry	Reaction conditions	Time (min)	Yield (%) <sup>a</sup>
1	Silica chloride, MeCN, reflux	360	93 <sup>10</sup>
2	Polyphosphoric acid–SiO <sub>2</sub> , neat, reflux	30	92 <sup>11</sup>
3	In(OTf) <sub>3</sub> , toluene, reflux	240	85 <sup>12</sup>
4	H <sub>2</sub> SO <sub>4</sub> , water, 70–80 °C	120	90 <sup>13</sup>
5	InCl <sub>3</sub> , solvent-free, 100 °C	36	83 <sup>14</sup>
6	CAN under ultrasound irradiation, 2-propanol, 50 °C	35	98 <sup>15</sup>
7	Succinimide- <i>N</i> -sulfonic acid, solvent-free, 80 °C	35	92 <sup>16</sup>
8	CaCl <sub>2</sub> , DMSO, 85–90 °C	240	85 <sup>17</sup>
9	Fe <sub>3</sub> O <sub>4</sub> nanoparticles, solvent-free, 100 °C	30	89 <sup>18</sup>
10	CAN supported HY-zeolite, solvent-free, 80 °C	90	88 <sup>19</sup>
11	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Imid-H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> , EtOH, reflux	150	82 <sup>20</sup>
12	Mg–Al hydrotalcite, H <sub>2</sub> O or EtOH, reflux	180	85 <sup>22</sup>
13	Thiourea dioxide, H <sub>2</sub> O, 50–60 °C	45	96 <sup>23</sup>
14	ZnO, H <sub>2</sub> O, reflux	20	94 <sup>24</sup>
15	MWCNT–BuSO <sub>3</sub> H, EtOH, r.t.	30	95

<sup>a</sup>Isolated yield.

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## Povzetek

Iz ustreznih izhodnih snovi smo enostavno pripravili nov katalizator sestavljen iz večstenskih ogljikovih nanocev z  $-SO_3H$  funkcionalnimi skupinami. Uporabili smo ga kot učinkovit heterogeni katalizator za enolončno Knoevenaglovo kondenzacijo, Michaelovo adicijo in ciklohidracijo 5,5-dimetil-1,3-cikloheksandiona (dimedona) z različnimi aromatskimi aldehidi. S pomočjo te metode smo z odličnimi izkoristki pri sobni temperaturi pripravili serijo 1,8-dioksoktahidroksantenov. Predstavljena metoda je boljša od že znanih glede na mnoge reakcijske parametre: reakcijsko temperaturo, reakcijski čas, postopek izolacije, izkoristek in ponovno uporabo katalizatorja.