

## SiO<sub>2</sub>@FeSO<sub>4</sub> NANO COMPOSITE AS NANOCATALYST FOR THE GREEN SYNTHESIS 1,1-DIACETATES FROM ALDEHYDES UNDER SOLVENT-FREE CONDITIONS

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### ABSTRACT

Aldehydes compounds selective converted to 1,1-diacetates as protective reagent with SiO<sub>2</sub>@FeSO<sub>4</sub> nano composite as effective nano catalyst at room temperature under solvent-free condition and acetic anhydride (Ac<sub>2</sub>O) as acetylation reagent. This method provides several advantages, such as low cost of the nano catalyst, high yields, short reaction time, chemoselective protection of aldehydes and operational simplicity. Aromatic and aliphatic, simple and conjugated aldehydes were protected with excellent yields. In addition, chemoselective reductive acetylation of aldehydes over ketones was achieved perfectly with the reagent at room temperature.

**Keywords:** Aldehydes, 1,1-Diacetates, SiO<sub>2</sub>@FeSO<sub>4</sub> catalyst, Acetic anhydride, Solvent-free

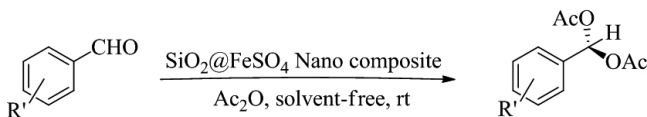
### 1. INTRODUCTION

The term nanotechnology is employed to describe the creation and exploitation of materials with structural features in between those of atoms and bulk materials, properties of materials of nanometric dimensions are significantly different from those of atoms as well as those of bulk materials.<sup>1</sup>

Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material. The properties of nano-composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics. Experimental work has generally shown that virtually all types and classes of nanocomposite materials lead to new and improved properties when compared to their macrocomposite counterparts.<sup>2,3</sup>

In organic reaction protection of functional groups during synthesis compounds are essential.<sup>4</sup> One of the important functional groups is aldehydes, because of easy converted to other organic groups for examples, alcohol,<sup>5</sup> carboxylic acids,<sup>6</sup> aldoximes,<sup>7</sup> moreover, the diacetates of  $\alpha,\beta$ -unsaturated aldehydes serve as an important precursor for Diels–Alder reactions. Some industrial uses of these compounds have also been reported.<sup>8</sup> Examples of the reagents and catalysts that have been developed for this purpose include Selectfluor<sup>TM</sup>,<sup>9</sup> MWCNTs-C-PO<sub>3</sub>H<sub>2</sub>,<sup>10</sup> PEG-SO<sub>3</sub>H,<sup>11</sup> Si-[SbSipim][PF<sub>6</sub>],<sup>12</sup> PS/TiCl<sub>4</sub>,<sup>13</sup> ZSM-5-SO<sub>3</sub>H,<sup>14</sup> [Ti(salophen)(OTf)<sub>2</sub>]<sup>15</sup> and [bmpy]HSO<sub>4</sub>.<sup>16</sup>

So in the course of our studies with nano catalyst<sup>7</sup> for effective synthesis, organic compound, we observed that 1,1-diacetates synthesis of aldehydes efficiently present of SiO<sub>2</sub>@FeSO<sub>4</sub> catalyst at solvent-free condition with high to excellent yield (Scheme 1). An important advantage of the use of SiO<sub>2</sub>@FeSO<sub>4</sub> catalyst is the possibility to use a small amount of catalyst.



R' = ary, alkyl, H (ref. table 2)

**Scheme 1.** Synthesis of 1,1-diacetates from aldehydes.

### 2. Experimental procedure:

#### 2.1. Chemicals and apparatus

All reagents and substrates were purchased from commercial sources with the best quality and used without further purification. SiO<sub>2</sub>@FeSO<sub>4</sub> catalyst was prepared with high purity according to the reported procedures in the literature.<sup>17</sup> IR spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 300 MHz Bruker Avance spectrometer in 300.13 an 75.46 MHz, respectively, and the X-ray powder diffraction (XRD) patterns were recorded using Philips APD-10 X-ray diffractometer with Cu K $\alpha$  radiation. All yields refer to isolated

pure products. TLC using silica gel 60 GF<sub>254</sub> aluminum sheet was applied for determination of the purity of substrates and products as well as monitoring the reaction.

#### Method1, typical experimental procedure for the preparation of 1,1-diacetates:

In a typical procedure, a mixture of benzaldehyde (106mg, 1mmol), Ac<sub>2</sub>O (306mg, 3 mmol) and SiO<sub>2</sub>@FeSO<sub>4</sub> catalyst (53mg, 0.25mmol) was stirred at room temperature for 10 min. After completion of the reaction, as indicated by TLC, diethylether was added and the mixture was washed successively with 1 M NaOH solution (10 mL), brine (10 mL) and H<sub>2</sub>O (10 mL). The organic layer was separated and dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation of the solvent under reduced pressure furnished almost pure product. Further purification was achieved by column chromatography (silica gel, ethylacetate: hexane = 1:9) or recrystallization from EOAc: hexane to afford a pure product in 98% yields (Table 2).

#### 2.2. Selected spectral data of the products:

**1,1-Diacetoxy-1-(2,4-dichlorophenyl)-methane (1).** solid: 85-87 °C; IR (KBr)  $\nu_{\max}$  3080, 3017, 2937, 1763, 1430, 1375, 1235, 1194, 1078 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.15 (s, 6H), 7.3-7.33 (m, 1H), 7.43 (s, 1H), 7.5-7.53 (d, j=8.4 Hz, 1H), 7.92 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.46MHz)  $\delta$  20.64, 86.64, 127.40, 128.73, 129.80, 132.01, 133.89, 136.23, 168.24.

**1,1-Diacetoxy-3-phenyl-2-propene (15).** solid: 84-86 °C; IR (KBr)  $\nu_{\max}$  3030, 2925, 1758, 1626, 1496, 1449, 1244, 1199, 1134, 1064, 997, 750, 692 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.12 (s, 6H), 6.18-6.26 (m, 1H), 6.85-6.9 (m, 1H), 7.31-7.55 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.46MHz)  $\delta$  20.89, 89.74, 121.72, 127.02, 128.68, 128.83, 129.07, 135.62, 168.75.

**1,1-Diacetoxy-1-naphthylmethane (16).** solid: 114-118 °C; IR (KBr)  $\nu_{\max}$  3058, 2926, 1762, 1693, 1372, 1238, 1208, 1098, 1051, 1011, 920, 808 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.16 (s, 6H), 7.47-7.68 (m, 3H), 7.73-7.75 (d, j=6.9 Hz, 1H), 7.87-7.93 (m, 2H), 8.27 (s, 1H), 8.29 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.46MHz)  $\delta$  20.90, 89.63, 124.14, 124.94, 126.03, 126.07, 126.98, 128.76, 130.29, 130.61, 130.84, 133.96, 168.77.

**1,1-Diacetoxy ethane (17).** Colorless liquid: 165–168 °C; IR (KBr)  $\nu_{\max}$  3465, 2984, 2937, 1762, 1433, 1374, 1243, 1123, 1084, 983, 917 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  1.28-1.30 (d, j=6.3 Hz, 3H), 1.86-2.17 (m, 6H), 6.85-6.89 (q, j=4.5 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.46MHz)  $\delta$  20.29, 20.80, 21.19, 87.84, 170.01.

### 3. RESULTS AND DISCUSSION

Herein, we wish to apply SiO<sub>2</sub>@FeSO<sub>4</sub> catalyst in protected aldehyde to 1,1-diacetates compounds under solvent-free condition.

Characterization of the SiO<sub>2</sub>@FeSO<sub>4</sub> nano composite was investigated by scanning electron microscopy (SEM). SEM image of the catalyst exhibited that the spherical nanoparticles dispersed well (Figure 1).

We first examined the acylation of benzaldehyde using Ac<sub>2</sub>O in the absence of SiO<sub>2</sub>@FeSO<sub>4</sub> catalyst. The reaction was sluggish and no corresponding 1,1-diacetate was formed even after many hours. However, in the presence

of 0.25 molar equivalent  $\text{SiO}_2@\text{FeSO}_4$  catalyst, the reaction progressed smoothly with benzaldehyde at room temperature to afford excellent yield of the corresponding 1,1-diacetate (Table 1 entry 2).

Likewise, we have applied this protocol for the protection of aliphatic, aromatic,  $\alpha$ ,  $\beta$ -unsaturated and phthalaldehyde and the results are summarized in Table 2. Both activated and deactivated aromatic aldehydes were converted to 1,1-diacetates. The tolerances of various functional groups have been examined by reacting the substrates with chloro, methyl, methoxy and nitro groups, and the reaction conditions are compatible with these functional groups.

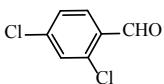
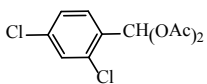
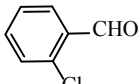
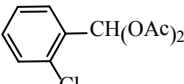
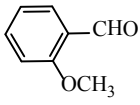
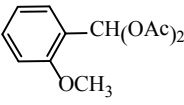
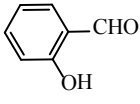
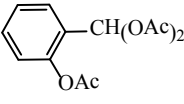
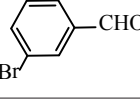
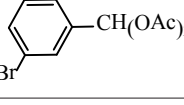
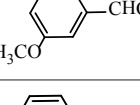
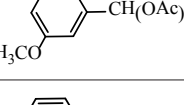
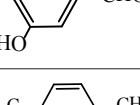
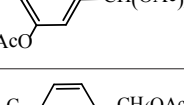
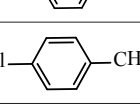
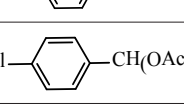
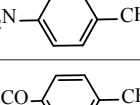
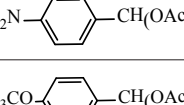
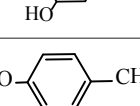
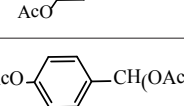


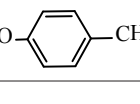
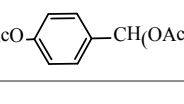
This protocol was then applied to protect naphthaldehydes. The yields of the corresponding 1,1-diacetates of naphthaldehydes (Table 2, entries 16) are good, although the time required for the completion of the reaction was longer compared to other aldehydes.

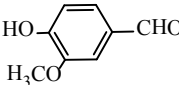
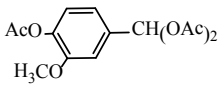
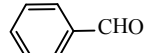
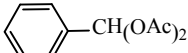
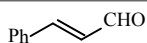
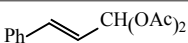
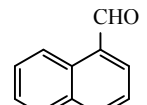
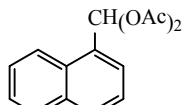

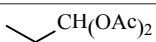
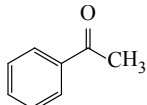
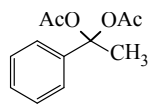


**Table 1.** Optimization of reaction condition for conversion of benzaldehyde to 1,1-diacetates with  $\text{SiO}_2@\text{FeSO}_4$  catalyst / $\text{Ac}_2\text{O}$  system.

Entry	Molar ratio <sup>a</sup>	Condition	Time (min)	Conversion (%)
1	1:0.25:1	Solvent-free/RT	30	25
2	1:0.25:3	Solvent-free/RT	5	100
3	1:0.25:5	Solvent-free/RT	5	100
4	1:0.25:1.5	Solvent-free/RT	8	100
5	1:0.25:2	Solvent-free/RT	5	100
6	1:1:2	Solvent-free/RT	30	15

<sup>a</sup> Benzaldehyde/  $\text{SiO}_2@\text{FeSO}_4$  catalyst / $\text{Ac}_2\text{O}$  molar ratio.

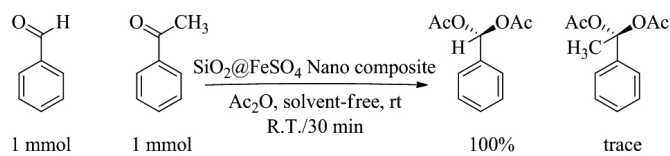
**Table 2.** Conversion of aldehydes to 1,1-diacetates with  $\text{SiO}_2@\text{FeSO}_4$  nano composite / $\text{Ac}_2\text{O}$  system <sup>a</sup>

En	Substrate	product	Molar ratio <sup>b</sup>	Time (min)	Yield (%) <sup>c</sup>	Mp.°C (Lit)	Ref.
1			1:0.25:3	4	98	87-89 (89)	[18]
2			1:0.25:3	5	98	57-59 (59)	[19]
3			1:0.25:3	5	98	194-195 (190-196)	[24]
4			1:0.25:4	5	96	101-103 (103-104)	[23]
5			1:0.25:3	5	98	83(85)	[24]
6			1:0.3:4	4	98	193(193)	[24]
7			1:0.45:4	6	97	98-99 (97-100)	[23]
8			1:0.25:3	4	98	80-82 (81-82)	[20]
9			1:0.25:3	6	98	81-83 (82-83)	[20]
10			1:0.25:2.5	4	98	124-126 (125-27)	[20]
11			1:0.5:3	4	98	105-107 (109-112)	[21]
12			1:0.4:3	6	98	89-90 (89-90)	[21]

13			1:0.45:3	4	97	90-91 (90-91)	[21]
14			1:0.25:3	5	98	42-44 (44-45)	[20]
15			1:0.6:3	4	96	83-85 (84-85)	[22]
16			1:0.35:4	4	96	116-118 (114-118)	[22]
17			1:0.40:3	4	96	Oil	---
18			1:2:4	30	NR	---	---
19			1:1:4	30	NR	---	---

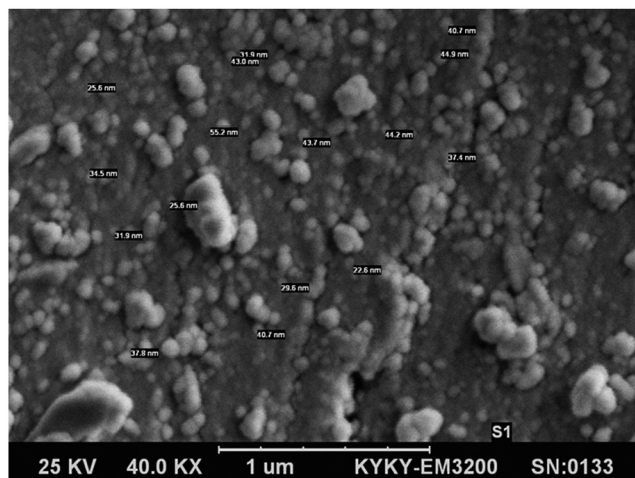
<sup>a</sup> all reaction were carried out under solvent-free conditions at RT; <sup>b</sup> Subs SiO<sub>2</sub>@FeSO<sub>4</sub> catalyst / Ac<sub>2</sub>O molar ratio; <sup>c</sup> yields refer to isolated pure.

As aldehydes are converted faster than ketones, this procedure affords chemoselective protection of aldehydes in the presence of ketones (Scheme 2).

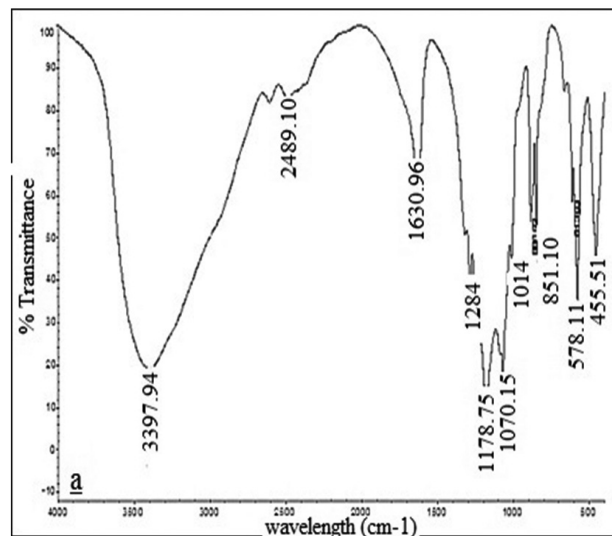


**Scheme 2.** Chemoselective synthesis acylal from aldehyde

A plausible mechanism for the SiO<sub>2</sub>@FeSO<sub>4</sub> catalyzed acetylation reaction was suggested. The nano catalyst facilitates the synthesis process through co-ordination with carbonyl of aldehyde and prompt carbonyl of acetic anhydride easy reaction.



**Figure1.** SEM image of synthesis SiO<sub>2</sub>@FeSO<sub>4</sub> nanoparticles.



**Figure2.** FT-IR spectra (KBr) of the synthesized SiO<sub>2</sub>@FeSO<sub>4</sub> catalyst.

In order to show the efficiency of this method, we compared our results with those reported in the literature as shown in Table 3.

**Table 3.** Comparison of conversion of aldehydes to 1,1-diacetates with SiO<sub>2</sub>@FeSO<sub>4</sub> catalyst /Ac<sub>2</sub>O system and other reported reaction systems.

En	system	condition	Time (min) /Yield(%)				
			benzaldehyde	4-hydroxy-benzaldehyde	4-nitro-benzaldehyde	Cinnamaldehyde	1-naphthaldehyde
1	(Selectfluor™) <sup>9</sup>	Solvent-free	70/86	---	45/84	---	60/80
		Microwave	5/99	---	7/94	---	15/85
2	MWCNTs-C-PO <sub>3</sub> H <sub>2</sub> <sup>10</sup>	Solvent-free	5/90	90/70	5/92	5/88	---
3	Nano SiO <sub>2</sub> Cl <sup>25</sup>	CH <sub>2</sub> Cl <sub>2</sub> /40°C	15/95	65/78	10/92	---	---
4	PEG-SO <sub>3</sub> H <sup>11</sup>	Solvent-free	15/89	15/88	15/97	---	---
5	Si-[SbSipim][PF <sub>6</sub> ] <sup>12</sup>	Solvent-free	180/90	240/86	---	---	---
6	PS/TiCl <sub>4</sub> <sup>13</sup>	CH <sub>2</sub> Cl <sub>2</sub>	40/93	50/88	75/84	40/89	---
7	ZSM-5-SO <sub>3</sub> H <sup>14</sup>	Solvent-free	1/95	---	4/97	---	---
		CH <sub>2</sub> Cl <sub>2</sub>	4/50	---	4/97	---	---
8	[Ti(salophen)(OTf) <sub>2</sub> ] <sup>15</sup>	CH <sub>3</sub> CN	---	---	---	---	---
9	[bmpy]HSO <sub>4</sub> <sup>16</sup>	Ultrasound	5/97	---	---	7/96	---
10	SiO <sub>2</sub> @FeSO <sub>4</sub> nano composite	Solvent-free	5/98	6/98	4/98	4/96	4/96

#### 4. CONCLUSION

In this paper, we have shown the application of SiO<sub>2</sub>@FeSO<sub>4</sub> catalyst for the efficient catalyzed synthesis of various 1,1-diacetates in high yields under solvent-free conditions. Simplicity, excellent yields, mildness and eco-friendly aspects of this synthetic protocol are the advantages which make this system an effective way to the present methodologies in this area.

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