

## SiO<sub>2</sub>@FeSO<sub>4</sub> nano composite: a recoverable nano-catalyst for eco-friendly synthesis oximes of carbonyl compounds

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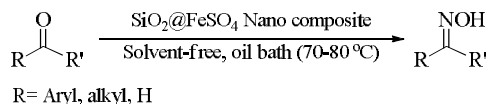
**ABSTRACT:** Various aldoximes and ketoximes synthesis of corresponding aldehydes and ketones in the presence of SiO<sub>2</sub>@FeSO<sub>4</sub> nano composite as recoverable nano catalyst and NH<sub>2</sub>OH·HCl. The SiO<sub>2</sub>@FeSO<sub>4</sub> nano composite system was carried out between 10 to 15 min in oil bath (70-80 °C) under solvent-free condition in excellent yields in addition this protocol can be used for industrial scales. This method offers some advantages in term of clean reaction conditions, easy work-up procedure, short reaction time, applied to convert α-diketones to α-diketoximes (as longer than other carbonyl compounds), α,β-unsaturated aldehydes and ketones to corresponding oximes and suppression of any side product. So we think that NH<sub>2</sub>OH·HCl/SiO<sub>2</sub>@FeSO<sub>4</sub> nano composite system could be considered a new and useful addition to the present methodologies in this area. Structure of products and nano composite elucidation was carried out by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, scanning electron microscopy (SEM).

**Keywords:** Carbonyl compound; SiO<sub>2</sub>@FeSO<sub>4</sub>; Nano composite; Solvent-free; Oxime

### INTRODUCTION

Nanoparticles have an extremely high surface to volume ratio, which dramatically change their properties when compared with their bulk sized equivalents. It also changes the way in which the nanoparticles bond with the bulk material. The result is that the composite can be many times improved with respect to the component parts. Some nano-composite materials have been shown to be 1000 times tougher than the bulk component materials [1]. Nanocomposites are currently being used in a number of fields and new applications are being continuously developed. Applications for nano composites include: Thermal stability [2], Chemical resistance [3], Optical clarity [4] and *etc.* Beside, application nano-composite as nano catalyst in organic synthesis provide unique chemical processes with special attributes such as enhanced reaction rates, eco-friendly condition, higher yields, greater selectivity and ease of manipulation [5].

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Scheme 1. A green and practical method for solvent-free conversion of various carbonyl compounds

In organic chemistry oxime is very important functional group as intermediate material for synthesis protocols, because of this, variety systems used catalyst for converted Nitro groups, alkyl groups, carbonyl groups and *etc.* to oximes [6].

Carbonyl compounds are a good convenient group for synthesis oximes and many catalysts as nano Fe<sub>3</sub>O<sub>4</sub> [7], Bi<sub>2</sub>O<sub>3</sub> [8], Cu-SiO<sub>2</sub> [9], TiO(acac)<sub>2</sub> [10] used. In continuing our attempted to apply nanocatalyst for synthesis oximes [7] for the first time in the world, we decided to synthesis oximes by nano composite as SiO<sub>2</sub>@FeSO<sub>4</sub>. We wish to report this nanocatalyst efficiently promotes the conversion of structurally different aldehydes and ketones to the corresponding (Scheme1).

## EXPERIMENTAL

### General

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> nanocomposite prepared in high purity according to the reported procedures in the literature [11]. Melting points were determined by Philip-Harris is melting point apparatus and are uncorrected. 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 and 75.46 MHz, SEM spectra were recorded on Philips XL30, respectively. 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.

### Preparation of Nano Catalyst [11]

The nano-composite was prepared by the sol-gel method. Briefly, FeSO<sub>4</sub>·H<sub>2</sub>O (0.85 g, 0.5 mmol) was dispersed in the mixture of ethanol (4 mmol), deionized water (4 mmol) and tetraethoxysilane (TEOS) (1 mmol), followed by the addition of 0.056 mmol of H<sub>2</sub>SO<sub>4</sub>. This solution was stirred mechanically for 60 min at room temperature. Then the product, SiO<sub>2</sub>@FeSO<sub>4</sub> nano-composite, was separated by filtered, and was washed with deionized water and ethanol three times and dried at 80 °C for 10 h.

### A Typical Procedure for Solvent-Free Oximation of Carbonyl Compounds to Corresponding Oxime with NH<sub>2</sub>OH·HCl/ SiO<sub>2</sub>@FeSO<sub>4</sub> Nano-Composite System. (Results are Presented in Table 2, 3)

A mixture of Substrate (1 mmol) and SiO<sub>2</sub>@FeSO<sub>4</sub> nano-composite (1 mmol) was ground in a mortar. NH<sub>2</sub>OH·HCl (2 mmol for aldehyde and 3 mmol for ketones) was then added to the mortar, and the grinding of the reaction mixture was continued for a moment. The mixture was stirred magnetically in oil bath (70-80 °C) under solvent-free conditions for reporting them. TLC monitored the progress of the reaction (eluent; n-hexane/EtOAc: 5/3). After completion of the reaction, the mixture was washed with EtOAc (3 × 5 ml). Evaporation of the solvent affords.

### A Typical Procedure for Reuse of the Nano Catalyst

SiO<sub>2</sub>@FeSO<sub>4</sub> nano-composite dissolved in solution is recovered after the reaction and separated from other products by washing with acetone and water (5 ml: 5 ml). The nano-composite is then dried in an oven at 110 °C overnight, and re-used up to four times in the same reaction without losing its activity.

### A Typical Procedure for Solvent-Free Oximation of Acetophenone to Acetophenone-Oxime with NH<sub>2</sub>OH·HCl/SiO<sub>2</sub>@FeSO<sub>4</sub> Nano-Composite System for up 1 g of Substrate

A mixture of Acetophenone (5 g) and SiO<sub>2</sub>@FeSO<sub>4</sub> nano-composite (2 g) was ground in a mortar. NH<sub>2</sub>OH·HCl (2.5 g) was then added to the mortar, and the grinding of the reaction mixture was continued for a moment. The mixture was stirred magnetically in oil bath (70- 80 °C) under solvent-free conditions for 10 min. TLC monitored the progress of the reaction (eluent; n-hexane/EtOAc: 5/3). After completion of the reaction, the mixture was washed with EtOAc (3 × 5 ml). Evaporation of the solvent affords the white solid Acetophenone Oxime in 90% yield (1215 g, Table 2: entry 1).white solid, m.p.: 58-60 °C. IR (KBr,  $\nu_{\max}$ ): 3235, 3084, 2924, 1496, 1444, 1370, 1300, 1079, 1005, 924, 847, 773, 756, 688 and 651 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 8.86 (br s, 1H), 7.69-7.58 (m, 2H), 7.43-7.36 (m, 3H), 2.32 (s, 3H), <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 156.1, 136.6, 129.3, 128.6, 126.1, 12.3; MS (EI) m/z (%rel. Intensity) 135 (M<sup>+</sup>, 86), 118 (14), 106 (22), 103 (26), 94 (32), 77 (100), 66 (16) and 51 (33).

## RESULTS AND DISCUSSION

The SiO<sub>2</sub>@FeSO<sub>4</sub> nanocomposite was synthesized by sol-gel method, Nano particles with 35 nm average diameter were characterized by SEM image as Fig. 1.

Comparing the FT-IR spectra of the synthesized SiO<sub>2</sub>@FeSO<sub>4</sub> nano particles (Fig. 2a) with the SiO<sub>2</sub> spectra (Fig. 2b) show the peaks at 1178 Cm<sup>-1</sup> for FeSO<sub>4</sub>.

Herein, we wish to apply SiO<sub>2</sub>@FeSO<sub>4</sub> nano-composite as efficient nano catalyst to convert carbonyl compounds to corresponding oximes at solvent-free condition. First, we examined the oximation of benzaldehyde using

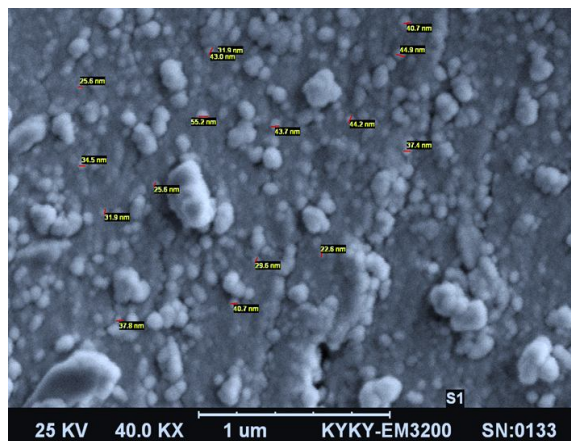


Fig. 1. SEM image of synthesis SiO<sub>2</sub>@FeSO<sub>4</sub> nanoparticles.

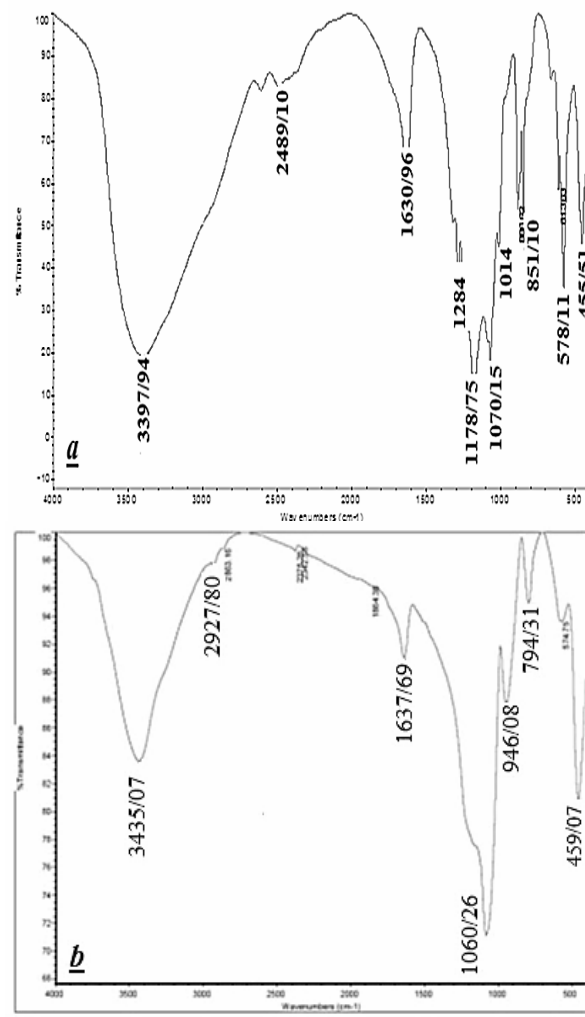


Fig. 2. FT-IR spectra of the synthesized SiO<sub>2</sub>@FeSO<sub>4</sub> nano particles (a) and the SiO<sub>2</sub> nano particles (b).

NH<sub>2</sub>OH•HCl in the absence of nanocomposite. The reaction was sluggish and no corresponding oximes were formed even after many minutes. However, in the presence of 1 molar equivalent SiO<sub>2</sub>@FeSO<sub>4</sub> nano-composite, the reaction progressed smoothly with benzaldehyde at oil bath (70-80

°C) to afford excellent yield of the corresponding oxime (Table 1 entry 2).

Likewise, we have applied this protocol for the oximation of aliphatic, aromatic,  $\alpha,\beta$ -unsaturated of aldehydes and ketones and the result summarized in Tables

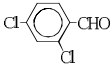
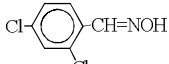
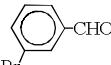
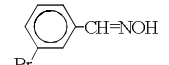
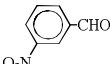
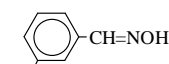
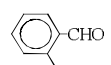
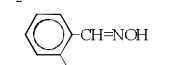
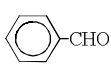
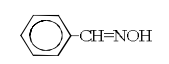
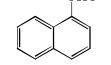
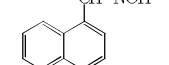
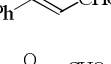
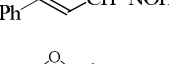
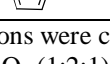
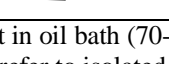
**Table 1.** Optimization Experiments for Oximation of Benzaldehyde with NH<sub>2</sub>OH•HCl/SiO<sub>2</sub>@FeSO<sub>4</sub> Nano Composite System under Different Reaction Conditions<sup>a</sup>

Molar ratio <sup>b</sup>	Condition <sup>c</sup>
1:2	Solvent-free/oil bath
1:2:1	Solvent-free/oil bath
1:1:1	Solvent-free/oil bath
1:2:2	Solvent-free/oil bath
1:3:1	Solvent-free/oil bath
1:2:1	Solvent-free/r.t.

<sup>a</sup>All reactions were carried out with 1 mmol of benzaldehyde. <sup>b</sup>Molar ratio as benzaldehyde/NH<sub>2</sub>OH•HCl/ SiO<sub>2</sub>@FeSO<sub>4</sub> Nano composite.

<sup>c</sup>Temperature of oil bath was (70-80 °C).

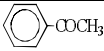
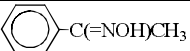
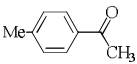
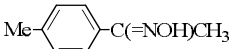
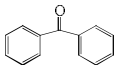
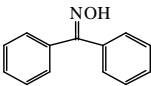

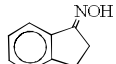

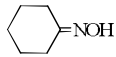
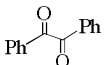
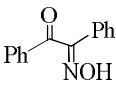
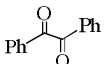

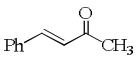
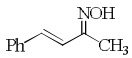
**Table 2.** Oximation of Aldehydes with NH<sub>2</sub>OH•HCl/SiO<sub>2</sub>@FeSO<sub>4</sub> Nano Composite System<sup>a, b</sup>

Entry	Substrate	Product	Time (min)	E:Z ratio <sup>c</sup>	R <sub>f</sub> <sup>d</sup>	Yield (%) <sup>e</sup>	Yield (%) <sup>f</sup>	M.p./°C (Lit.)
1			10	98:2	0.45	98	88	134 (136)[12]
2			10	98:2	0.25	98	90	98 (98-100)[15]
3			10	96:4	0.45	98	89	121 (122)[12]
4			10	98:2	0.25	99	97	75 (73-76) [12]
5			12	97:3	0.50	98	96	- (30-33)[12]
6			15	98:2	0.40	95	90	155 (156)[12]
7			10	98:2	0.35	94	88	136 (139)[12]
8			11	98:2	0.25	96	80	74 (75-76) [12]

<sup>a</sup>All reactions were carried out in oil bath (70-80 °C) under solvent-free conditions. <sup>b</sup>Molar ratio as Subs./NH<sub>2</sub>OH•HCl/SiO<sub>2</sub>@FeSO<sub>4</sub> (1:2:1). <sup>c</sup>Yields refer to isolated pure products. <sup>d</sup>Retention Factor (The location of each spot on the TLC).

<sup>e</sup>Approximately determined from TLC. <sup>f</sup>Yields refer to isolated pure products from 5 g substrate.

**Table 3.** Oximation of Ketones with NH<sub>2</sub>OH·HCl/SiO<sub>2</sub>@FeSO<sub>4</sub> Nano Composite System<sup>a, b</sup>

Entry	Substrate	Product	Time (min)	E:Z ratio <sup>c</sup>	R <sub>f</sub> <sup>d</sup>	Yield (%) <sup>e</sup>	Yield (%) <sup>f</sup>	M.p./°C (Lit.)
1			10	98:2	0.40	99	90	58 (58-60)[14]
2			14	98:2	0.35	97	95	85 (84-86)[14]
3			12	100	0.45	98	92	142 (144)[12]
4			12	98:2	0.50	96	90	148 (150)[12]
5			10	100:0	0.45	97	98	88 (91)[12]
6			12	100:0	0.24	98	90	108(153-155)[12]
7			15	100:0	0.38	99	98	242 (243-245)[12]
8			10	97:3	0.25	97	89	118 (116- 120)[12]

<sup>a</sup>All reactions were carried out in oil bath (70-80 °C) under solvent-free conditions. <sup>b</sup>Molar ratio as Subs./NH<sub>2</sub>OH·HCl/SiO<sub>2</sub>@FeSO<sub>4</sub> (1:3:2). <sup>c</sup>Yields refer to isolated pure products. <sup>d</sup>Retention Factor (The location of each spot on the TLC). <sup>e</sup>Approximately determined from TLC. <sup>f</sup>Yields refer to isolated pure products from 5 g substrate.

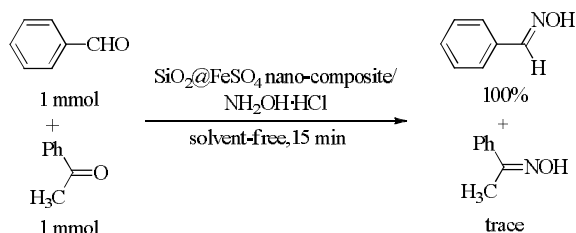
2 and 3. Both activated and deactivated aromatic aldehydes and ketones were converted to corresponding oximes. The tolerances of various functional groups have been examined by reacting the substrates with chloro, methyl, methoxy and Nitro groups, and the reaction conditions are compatible with these functional groups.

This protocol also applied to convert  $\alpha$ -diketones. The yields of the corresponding oximes of  $\alpha$ -diketones (Table 3) are good, although required time for completion of the reaction was longer than other carbonyl compounds. In addition, we applied the report of our method for converting of five grams of some carbonyl compound used in this protocol and the result shown in the Tables 2 and 3.

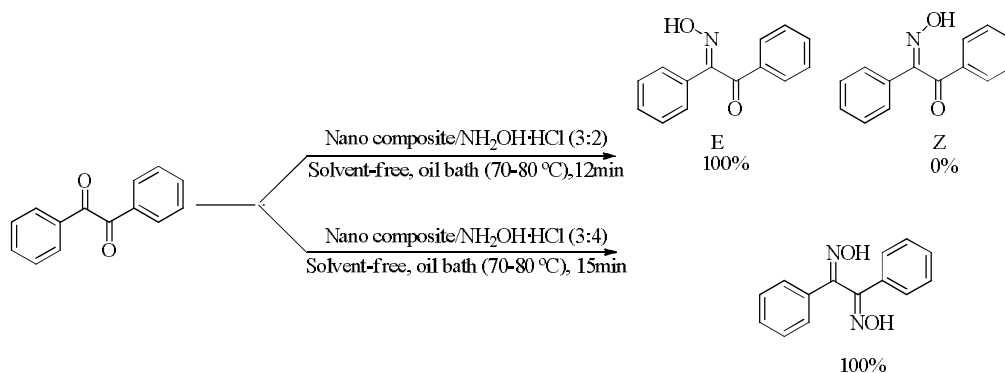
To continue, we compared oximation of aldehydes with ketones at the same condition, as the result shown aldehydes converted faster than ketones, this procedure affords

chemoselective convert of aldehydes in the presence of ketones (Scheme 2). As oximation of compounds with two carbonyl groups was carried out selectively on one carbonyl moiety (Scheme 3). In order to show the efficiency of this method, we compared our results with other reported in literature as shown in Table 4.

(Z)-oximes and (E)-oximes can be separated on a silica gel TLC plate. Although they are both colorless, ultraviolet light will reveal their positions on a TLC plate. TLC (or thin layer chromatography) is performed on a glass plate which is coated with a thin layer of silica. The small amount of the mixture to be analyzed is loaded near the bottom of this plate. The TLC plate, then placed in a shallow pool of a solvent in a developing chamber so that only bottom of the plate is in the liquid. This liquid slowly rises up the TLC plate by capillary action, when the solvent has reached the



Scheme 2



Scheme 3

**Table 4.** Comparison of Conversion of Carbonyl Compounds to Oximes with  $\text{SiO}_2\text{@FeSO}_4$  Nano-Composite/ $\text{NH}_2\text{OH}\cdot\text{HCl}$  System and other Reported Reaction Systems

Entry	System	Condition	Molar ratio (reagent/substrate), Time (min), Yield (%)			
			Acetophenone	Benzil	Cinnamaldehyde	Furfural
1[7]	Nano $\text{Fe}_3\text{O}_4$	Solvent-free	2, 60, 90	2, 180, 95	1.5, 50, 92	2, 15, 74
2[8]	$\text{Bi}_2\text{O}_3$	Solvent-free	1.2, 7, 98	-	1.2, 2, 98	1.2, 2, 95
3[10]	$\text{TiO}(\text{acac})_2$	$\text{CH}_3\text{CN}$	3, 120, 85	-	2, 43, 93	-
4[9]	$\text{Cu-SiO}_2$	Aq.EtOH	-	-	1.5, 120, 90	1.5, 120, 90
5	$\text{SiO}_2\text{@FeSO}_4$ Nano-composite	Solvent-free	3, 10, 99	3, 15, 99	2, 10, 94	2, 11, 96

top of the plate; the plate is removed from the developing chamber, dried and investigated ultraviolet light.

In case of aldoximes, the syn form is the one in which both the hydrogen and the hydroxyl (-OH) group are on the same side of the C=N (1). Whereas in the anti-form, they are on the opposite side (2). Selectivity in oximation of aldehydes with  $\text{SiO}_2\text{@FeSO}_4$  nano-composite is a perfect

and the corresponding E isomer of aldoximes were obtained in high with excellent yields (Table 1).

However, with ketoximes, the geometrical isomers are better differentiated by using E-Z notations. The Z ketoxime has hydroxyl group and the group with higher priority on the same side of C=N (3). However, in the E ketoxime, they are arranged on the opposite sides of the C=N (4).

## CONCLUSIONS

In this paper, we have shown SiO<sub>2</sub>@FeSO<sub>4</sub> Nano composite promoted oximation of various carbonyl compounds by hydroxylamine hydrochloride in oil bath (70-80 °C) under solvent-free conditions. aldoximes and ketoximes were obtained in high yields within 10 to 15 min. This method offers some advantages in term of clean reaction conditions, easy work-up procedure, short reaction time, and suppression of any side product. So we think that NH<sub>2</sub>OH•HCl/SiO<sub>2</sub>@FeSO<sub>4</sub> Nano composite system could be considered a new and useful addition to the present methodologies in this area.

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