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Magnetic Fe₃O₄ nanoparticles as recovery catalyst for preparation of oximes under solvent-free condition

Behzad Zeynizadeh and Mostafa Karimkoshteh*

Abstract

Magnetically nano Fe₃O₄ efficiently catalyzes solvent-free conversion of various carbonyl compounds to the corresponding oximes with NH₂OH·HCl. The reactions were carried out in oil bath (70°C to 80°C) at solvent-free conditions to afford oximes in high to excellent yields. This method offers some advantages in terms of clean reaction conditions, recyclable of catalyst, short reaction times, easy work-up procedure, and suppression of side products.

Keywords: Carbonyl compounds; Nano Fe₃O₄; Magnetic; NH₂OH·HCl; Oxime

Background

Transformation of carbonyl compounds into oximes is one of the most important synthetic reactions in organic chemistry. Oximes are not only useful for protection, purification, and characterization of carbonyl compounds [1] but also they can serve as intermediates for conversion into nitro compounds [2], amides [3], nitriles [4], and amines [5]. In addition, all compounds that contain the oxime fragment, which represents a pharmacophore group, exhibit diverse biological activities. These derivatives are also recommended as insecticides, fungicides, pesticides, herbicides, protozoacides, and plant growth regulators [6]. A wide spectrum of biological activity was revealed for oximes of pyridine, indole, isatin, and pyrrole and quinoline series [7]. Oximes of α , β -unsaturated ketones are known as insecticides, vasorelaxants, and antimicrobial agents [6].

The literature review shows that many improvements have been carried out for the preparation of oximes. NH₂OH·HCl/K₂CO₃ [8], DOWEX(R)50WX4 [9], ethylenediamine/oxone [10], ultrasound/Na₂SO₄ [11], Bi₂O₃ [12], heterogeneous polyoxometalates [13], phase transfer catalysis [14], and TiO(acac)₂ [15] are some of the

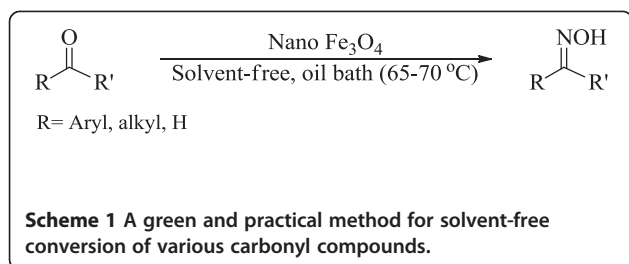
reagents or protocols which have been reported for transformation of carbonyl compounds to oximes. Generally low yields, long reaction times, and limitation to use acid- or base-sensitive functionality in carbonyl compounds are the major limitations of these methods.

On the other hand, nanoparticles exhibit high catalytic activity and chemical selectivity under mild conditions [16]. The extremely small-size particles maximize the surface area which, when exposed to the reactant, allow more reactions to occur at the same time and thus speed up the process [17]. Thus, in the line of the outlined strategies, herein, we wish to report a green and practical method for solvent-free conversion of various carbonyl compounds to the corresponding oximes by NH₂OH·HCl catalyzed by magnetically nano Fe₃O₄ (Scheme 1).

Results and discussion

Magnetically nano Fe₃O₄ due to highly active and specific centers of ultra-size coupled with high magnetic specification has been found some useful applications in organic synthesis [18]. Continuation of our research program directed to the oximes reactions under mild and green reaction conditions [3] and lack of information to use magnetically nano Fe₃O₄ in preparation of oximes from carbonyl compounds by NH₂OH·HCl encouraged us to investigate the titled transformation.

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The promotion effect of nano Fe_3O_4 in the formation of oximes was studied by the reaction of benzaldehyde with $\text{NH}_2\text{OH}\cdot\text{HCl}$ under different reaction conditions. The effects of molar ratio of the reaction components and solvent were investigated in the typical experiment (Table 1). As it is seen, the combination system of hydroxylamine hydrochloride with nano Fe_3O_4 in a molar ratio of 2:1.5, respectively, in oil bath (70°C to 80°C) at solvent-free conditions showed a perfect efficiency for complete conversion of 1 mmol benzaldehyde to benzaldehydeoxime within 20 min (entry 6). This success encouraged us to further explore the capability of $\text{NH}_2\text{OH}\cdot\text{HCl}$ /nano Fe_3O_4 system for oximation of different carbonyl compounds at the optimized reaction conditions. The summarized results in Tables 2 and 3 show that all reactions were carried out successfully in oil bath (70°C to 80°C) at solvent-free conditions, and the corresponding aldoximes or ketoximes were obtained in high to excellent yields within 15 min to 3 h. In addition, due to inherent less reactivity of ketones versus aldehydes, the oximation reactions took excess amounts of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and nano Fe_3O_4 in longer reaction times (Table 3). α,β -Unsaturated aldehydes and ketones were successfully converted to the corresponding conjugated oximes with $\text{NH}_2\text{OH}\cdot\text{HCl}$ /nano Fe_3O_4 system in high yields and without any side reaction (Table 2: entry 8 and Table 3: entry 9). We also observed that oximation of carbonyl compounds with two carbonyl moieties was carried out selectively. By using the controlled amounts of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in an appropriate time, oximation of one or both of the carbonyl group took place efficiently (Table 3: entries 7 and 8).

A plausible mechanism for the nano Fe_3O_4 catalyzed was illustrated in Scheme 2. The nano Fe_3O_4 facilitates the oximation process through coordination of its Fe^{3+} with O of carbonyl.

In the next attempt, we turned our attention to recyclable of catalyst; the catalyst was easily separated from the reaction system and reused (after washing with distilled water/acetone and dried under vacuum) for three consecutive runs, and no obvious diminishing activity was observed (the conversions and selectivities were 100% and 100% for first run; 99% and 100% for

second run; 91% and 95% for third run; 91% and 90% for fourth run).

Conclusions

In this paper, we have shown that magnetically nano Fe_3O_4 promoted oximation of various carbonyl compounds by hydroxylamine hydrochloride in oil bath (70°C to 80°C) under solvent-free conditions. Aldoximes and ketoximes were obtained in high yields within 15 min to 3 h. This method offers some advantages in term of clean reaction conditions, easy work-up procedure, short reaction times, and suppression of any side product. So we think that $\text{NH}_2\text{OH}\cdot\text{HCl}$ /nano Fe_3O_4 system could be considered a new and useful addition to the present methodologies in this area.

Methods

General

All solvents and reagents were purchased from commercial sources with the best quality and they were used without further purification. Nano Fe_3O_4 are prepared in high purity according to the reported procedures in literature [19] (Figures 1, 2, and 3). ^1H , ^{13}C NMR, and IR spectra were recorded on 300 MHz Bruker Avance and Thermo Nicolet Nexus 670 FT-IR spectrometers (Bruker AXS, Inc., Madison, WI, USA). All products are known and were characterized by their spectral data. Yields refer to isolated pure products. Thin layer chromatography (TLC) was applied for monitoring of the reactions over silica gel 60 F_{254} aluminum sheet.

A typical procedure for solvent-free oximation of acetophenone to acetophenone-oxime with $\text{NH}_2\text{OH}\cdot\text{HCl}$ /nano Fe_3O_4 system

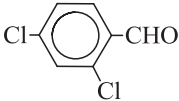
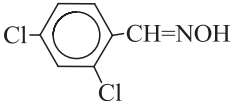
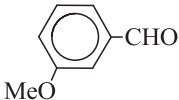
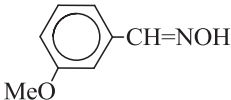
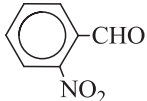
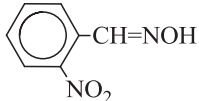
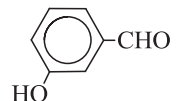
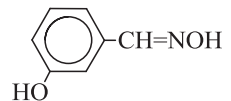
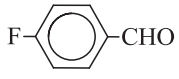
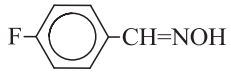

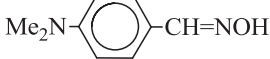


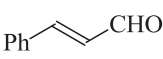
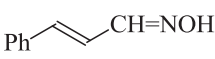
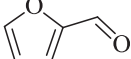
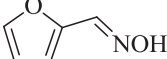
A mixture of Acetophenone (0.120 g, 1 mmol) and nano Fe_3O_4 (0.462 g, 2 mmol) was ground in a mortar.

Table 1 Optimization experiment for oximation of benzaldehyde with $\text{NH}_2\text{OH}\cdot\text{HCl}$ /nano Fe_3O_4 system under different reaction conditions (all reactions were carried out with 1 mmol of benzaldehyde)

Entry	Molar ratio ^a	Condition ^b	Time (min)	Conversion (%)
1	1:2:1.5	$\text{CH}_3\text{CH}/\text{reflux}$	120	30
2	1:2:1.5	$\text{EtOH}/\text{reflux}$	100	30
3	1:2:1.5	$\text{H}_2\text{O}/\text{reflux}$	120	60
4	1:2:1.5	THF/reflux	100	10
5	1:2:1	Solvent-free/oil bath	50	80
6	1:2:1.5	Solvent-free/oil bath	20	100
7	1:2:2	Solvent-free/oil bath	20	100

^aMolar ratio as benzaldehyde/ $\text{NH}_2\text{OH}\cdot\text{HCl}$ /nano Fe_3O_4 ; ^btemperature of oil bath was (70° to 80°C).

Table 2 Oximation of aldehydes with NH₂OH·HCl/nano Fe₃O₄ system (all reactions were carried out in oil bath (70°C to 80°C) under solvent-free conditions)

Entry	Substrate	Product	Molar ratio ^a	Time (min)	E:Z ratio ^b	Yield (%) ^c
1			1:2:1.5	15	98:2	96
2			1:2:1.5	30	98:2	95
3			1:2:1.5	25	96:4	95
4			1:2:1.5	30	98:2	96
5			1:2:1.5	20	98:2	98
6			1:2:1.5	15	97:3	93
7			1:3:1.5	45	98:2	90
8			1:2:1.5	50	98:2	92
9			1:2:2	15	100	74

^aMolar ratio as Subs./NH₂OH·HCl/nano Fe₃O₄; ^bapproximately determined from TLC; ^cyields refer to isolated pure products.

NH₂OH·HCl (0.2085 g, 3 mmol) 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°C to 80°C) under solvent-free conditions for 60 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°C to 60°C. IR (KBr, ν_{\max}): 3,235, 3,084, 2,924, 1,496, 1,444, 1,370, 1,300, 1,079, 1,005, 924, 847, 773, 756, 688, and 651 cm⁻¹. ¹H NMR

(300 MHz, CDCl₃, δ ppm): 8.86 (br s, 1H), 7.69 to 7.58 (m, 2H), 7.43-7.36 (m, 3H), 2.32 (s, 3H), ¹³C NMR (75 MHz, CDCl₃, δ ppm): 156.1, 136.6, 129.3, 128.6, 126.1, 12.3; MS (EI) *m/z* (% rel. intensity) 135 (M⁺, 86), 118 (14), 106 (22), 103 (26), 94 (32), 77 (100), 66 (16), and 51 (33).

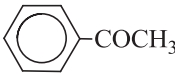
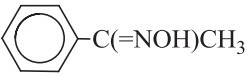
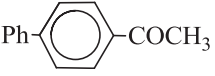
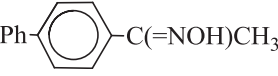
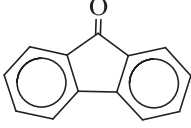
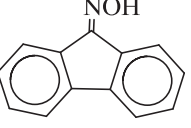
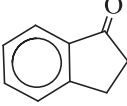
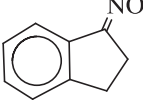
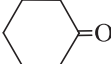
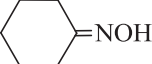
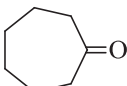
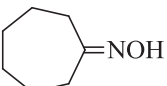
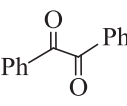
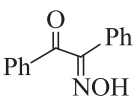
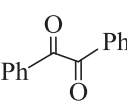
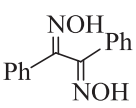
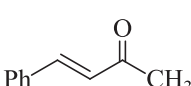
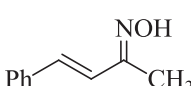
Competing interests

Both authors declare that they have no competing interests.

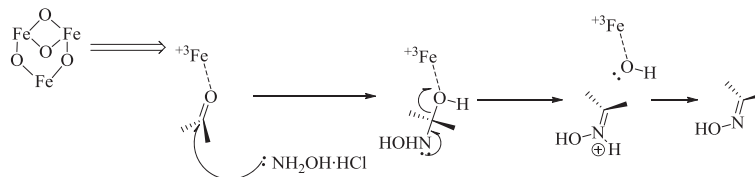
Authors' contributions

BZ participated in the design of the study and performed the statistical analysis. MK carried out the nanoparticle studies and participated in its design and coordination. Both authors read and approved the final manuscript.

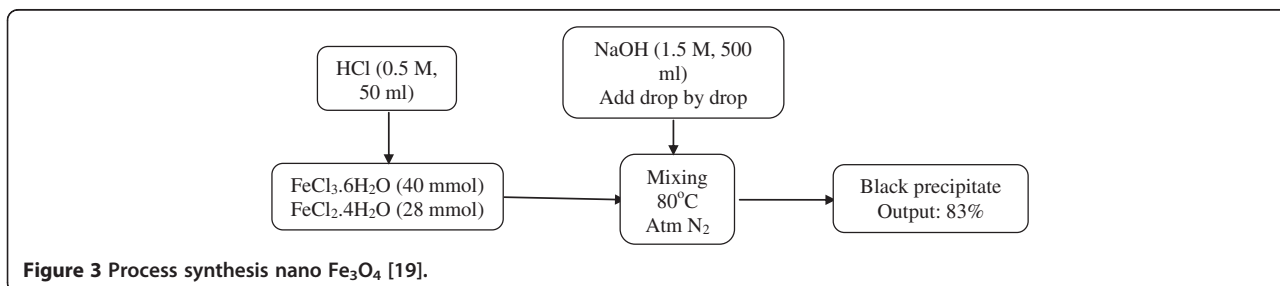
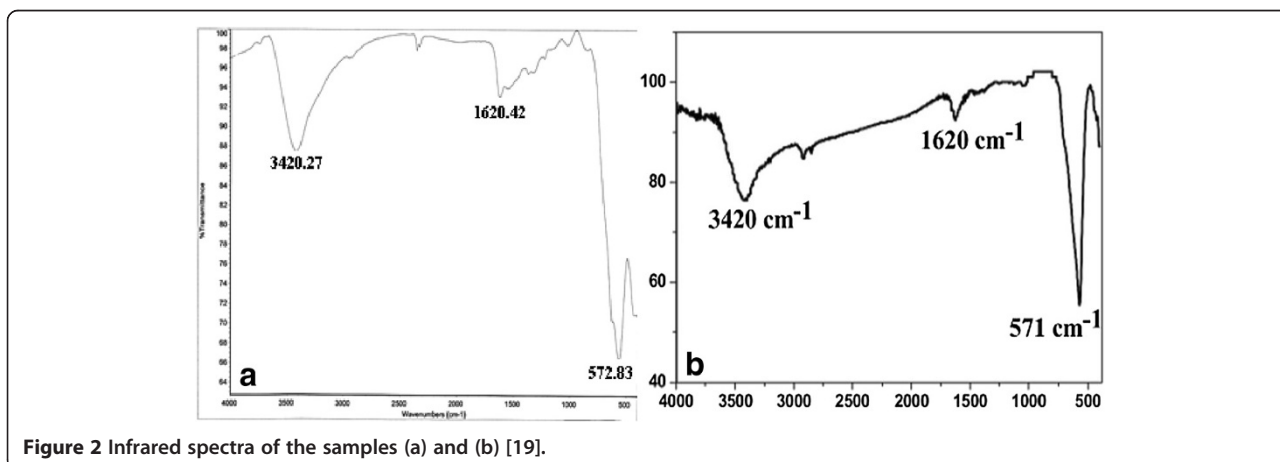
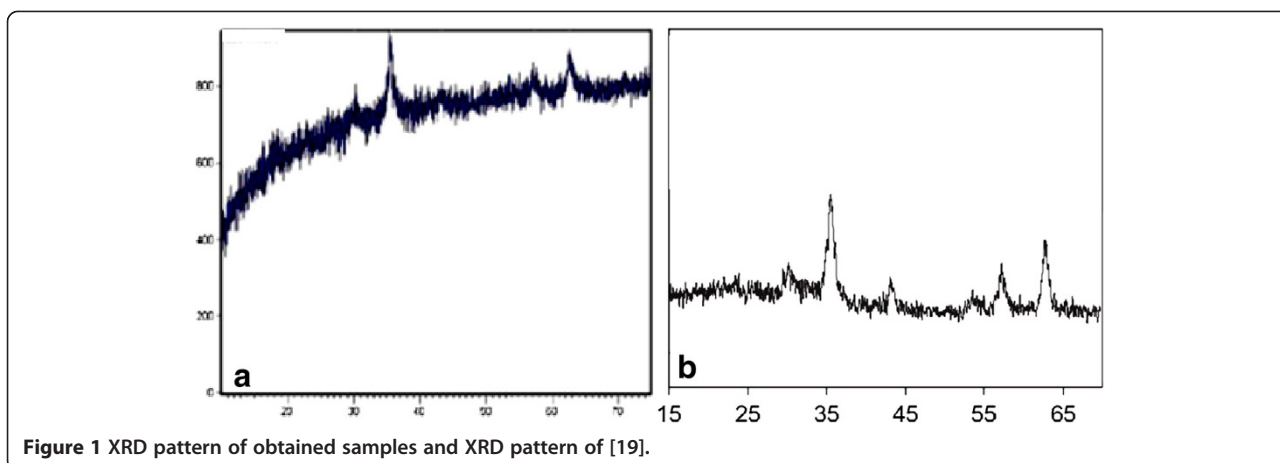
Table 3 Oximation of ketones with NH₂OH-HCl/nano Fe₃O₄ system (all reactions were carried out oil bath (70°C to 80°C) under solvent-free conditions)

Entry	Substance	Product	Molar ratio ^a	Time (h)	E:Z(%) ^b	Yield (%) ^c
1			1:3:2	1	98:2	90
2			1:3:2	1.8	98:2	94
3			1:3:2	2	100:0	93
4			1:3:2	1.8	98:2	95
5			1:3:2	1.2	100:0	94
6			1:3:2	1	100:0	92
7			1:3:2	2.2	100:0	93
8			1:4:2	3	100:0	95
9			1:3:2	3	96:4	95

^aMolar ratio as Subs./NH₂OH-HCl/nano Fe₃O₄; ^bapproximately determined from TLC; ^cyields refer to isolated pure products.



Scheme 2 A plausible mechanism for the nano Fe₃O₄ catalyzed.



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References

1. Mikhaleva, IA, Zaitsev, AB, Trofimov, BA: Oximes as reagents. *Russ Chem Rev* **75**, 797–823 (2006)
2. Barnes, MW: An oxime to nitro conversion. a superior synthesis of secondary nitroparaffins. *J Org Chem* **41**, 733–735 (1976)
3. Bagheri, M, Karimkoshteh, M: Nano SiO₂/H₂SO₄ as catalyst for the Beckmann rearrangement and deoxygenation of aldioximes. *IJC* **3**(1), 27–32 (2013)
4. Hegedüs, A, Cwik, A, Hell, Z, Horváth, Z, Esek, A, Uzsoki, M: Microwave-assisted conversion of oximes into nitriles in the presence of a zeolite. *Green Chem* **4**, 618–620 (2002)
5. Zeynizadeh, B, Kouhkan, M: A rapid and practical protocol for solvent-free reduction of oximes to amines with NaBH₄/ZrCl₄/Al₂O₃ system. *Bull Korean Chem Soc* **32**, 3448–3452 (2011)
6. Abele, E, Lukevics, E: Recent advances in the chemistry of oximes. *Org Prep Proced Int* **32**, 235–264 (2000)
7. Abele, E, Lukevics, E: Recent advances in the synthesis of heterocycles from oximes. *Heterocycles* **53**, 2285–2336 (2000)
8. Bo, RK, Gi, HS, Jeum, JK, Yong, JY: A development of rapid, practical and selective process for preparation of Z-oximes. *J Korean Chem Soc* **57**, 295–299 (2013)
9. Davood, S, Behrooz, K, Seyran, E: Synthesis of oximes with NH₂OH·HCl/DOWEX(R) 50W-X4 system. *J Chin Chem Soc* **59**, 1119–1124 (2012)
10. Xia, JJ, Wang, GW: Efficient preparation of aldioximes from arylaldehydes, ethylenediamine and Oxone® in water. *Molecules* **12**, 231–236 (2007)
11. Li, JT, Li, XL, Li, TS: Synthesis of oximes under ultrasound irradiation. *Ultrason Sonochem* **13**, 200–202 (2006)
12. Lakhinath, S, Jejiron, MB, Ashim, JT: A rapid, convenient, solventless green approach for the synthesis of oximes using grindstone chemistry. *Org Med Chem Lett* **1**, 12 (2011)
13. Shen, Z, Lujiang, H, Yu-Fei, S: Highly selective and efficient Lewis acid–base catalysts based on lanthanide-containing polyoxometalates for oximation of aldehydes and ketones. *Eur J Inorg Chem* **2013**, 1659–1663 (2013)
14. Tomilov, AP, Osadchenko, M: Phase-transfer catalysis in synthesis of oximes. *Russ J Appl Chem* **75**, 511–512 (2002)
15. Zeynizadeh, B, Amjadi, E: Facile Oximation of carbonyl compounds with titanium acetylacetonate/NH₂OH system. *Asian J Chem* **21**, 3611–3616 (2009)
16. Nasir Baig, RB, Rajender, SV: Magnetically retrievable catalysts for organic synthesis. *Chem Commun* **49**, 752–770 (2013)
17. Montazeri, H, Amani, A, Shahverdi, HR, Haratifar, E, Shahverdi, AR: Separation of the defect-free Fe₃O₄-Au core/shell fraction from magnetite-gold composite nanoparticles by an acid wash treatment. *J Nanostruct Chem* **3**, 25 (2013)
18. Polshettiwar, V, Luque, R, Fihri, A, Zhu, H, Bouhrara, M, Basset, JM: Magnetically recoverable nanocatalysts. *Chem Rev* **111**, 3036–3075 (2011)
19. Ch, MX, Cui, LH, Xu, GF: The preparation of Fe₃O₄ magnetic nanometer particle by co-precipitation. *Method* **320**, 271–272 (2012)

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