

One-Pot Reduction of Aromatic Carboxylic Acid to Alcohol by SiO₂@FeSO₄ Nano Composite at Solvent-free Condition

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ABSTRACT: Application of SiO₂@FeSO₄ nano composite as a new nano catalyst in reduction area was investigated. Carboxylic acid simple and convenient reduction to alcohol by 0.75 mol of the nano composite, 3 mol sodium borohydride (NaBH₄) as reduction reagent under solvent free condition at 30-65 min. The reaction happens in two stages - first to form an aldehyde and then a primary alcohol. Because sodium aluminum hydride reacts rapidly with aldehydes, it is impossible to stop at the halfway stage. The method does not require an anhydrous solvent, does not involve a hazardous reagent, has somewhat different selectivity than techniques in general use, and may sometimes be the method of choice.

KEYWORDS: SiO₂@FeSO₄; Carboxylic acid, Alcohol; NaBH₄; Solvent-free.

INTRODUCTION

The field of nanoscience has opened up new areas of interest for the construction of interesting and novel catalytic systems [1]. Nanoscale materials make ideal catalytic materials in many ways. Because of two reasons: First, their extremely small size yields a tremendous surface area to volume ratio [2]. Also, when materials are fabricated at the nanoscale, they achieve properties not found within their macroscopic counterparts. Both of these reasons accounts for the versatility and effectiveness of nano catalysts [3,4].

The selective reduction of carboxylic acids to alcohols is an important transformation in synthetic organic chemistry [5-7] and several reagents will carry out this

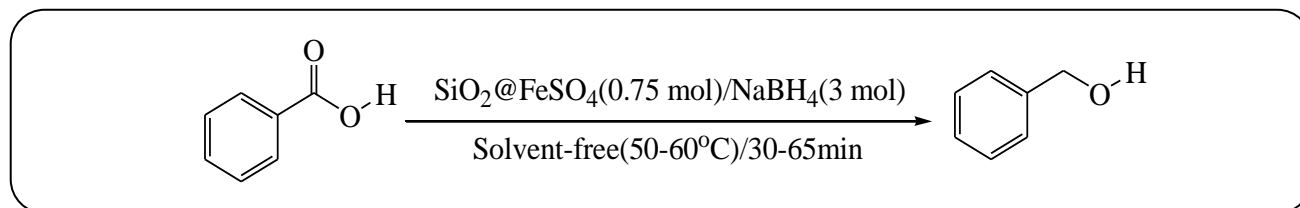
reaction, for example, lithium aluminium hydride, boranes or modified sodium borohydride [8-11]. Sodium borohydride was used as reducing agent for this purpose, but carboxylic acid could not be reduced individually by sodium borohydride [12, 13]. In order to increase the reactivity of sodium borohydride, various additives were used. Several methods are available for this purpose that utilizes Raney nickel/NaBH₄ [14], PPh₃/K₂CO₃/NaBH₄ [15], PNT/NMM/NaBH₄ [16]. However, some of these methods suffer from different disadvantages such as tedious work-up procedure, drastic reaction conditions, long reaction times, undesired chemical yields and use of expensive and toxic reagents.

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Scheme 1: Reduction aromatic carboxylic acids to alcohols.

Therefore, a milder, more selective, non-hazardous and inexpensive reagent is still required for such transformation. We report here that carboxylic can be reduced to alcohols by NaBH_4 with $\text{SiO}_2@\text{FeSO}_4$ nano catalyst under solvent-free condition (Scheme1).

EXPERIMENTAL SECTION

Chemicals and apparatus

All reagents and substrates were purchased from commercial sources with the best quality and used without further purification. $\text{SiO}_2@\text{FeSO}_4$ nano catalyst prepared in high purity according to the reported procedures in the literature [17]. 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. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz Bruker Avance spectrometer in 300.13 and 75.46 MHz, XRD and SEM spectra were recorded on Philips X'pert PW3040/60 and Philips XL30, respectively. All yields refer to isolated pure products. TLC using silica gel 60 GF₂₅₄ aluminum sheet was applied for determination of the purity of substrates and products as well as monitoring the reaction.

A typical procedure for one put the reduction of carboxylic acids to alcohol under solvent free condition

A mixture of cinnamyl acid (0.148 g, 1 mmol) and nano composite (0.158 g, 0.75 mmol) was ground in a mortar. NaBH_4 (0.114 g, 3 mmol) was added portion wisely to the mortar, and the grinding of the reaction mixture was continued for a few minutes. Then, the grinding was continued for about 65 min. at 50°C to 60°C under solvent-free conditions. After completion of the reaction (TLC), the residue was taken up in diethyl ether (50 mL), washed with saturated NaHCO_3 (3×10 mL) and brine (10 mL). After drying over anhydrous Na_2SO_4 , the ether was evaporated to give the product. The product

was purified by column chromatography (silica gel, ethyl acetate: petroleum ether, 1:9). Evaporation of the solvent affords the cinnamyl alcohol in 85% yield (Table 2: entry 10).

Selected spectral data of the products:

(4-Aminophenyl) methanol (Table2, entry2). ^1H NMR (CDCl_3 , 300 MHz) δ 1.82 (bs, 1H, OH), 3.59 (bs, 2H, NH_2), 4.55 (s, 2H, CH_2), 6.68 (d, $J=8.1$ Hz, 2H, Ar), 7.164 (d, $J=7.8$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 65.27, 115.13, 128.76, 131.07, 138.7; FT-IR ($\nu_{\text{max}}/\text{cm}^{-1}$, neat) 3377, 3229, 2874, 1618, 1514, 1467, 1257, 1041, 824, 510.

(3-Aminophenyl) methanol (Table 2, entry4). ^1H NMR (CDCl_3 , 300 MHz) δ 2.96 (bs, 3H, $\text{NH}_2\&\text{OH}$), 4.60 (s, 2H, CH_2), 6.62 (s, 1H, Ar), 6.74 (m, 2H, Ar), 7.15 (t, $J=7.5$ Hz, 1H, Ar); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 65.359, 113.561, 114.396, 117.094, 129.519, 142.249, 146.634.; IR ($\nu_{\text{max}}/\text{cm}^{-1}$, neat) 2963, 1744, 1436, 1371, 1221, 1046.

(2-Aminophenyl) methanol (Table 2, entry3). ^1H NMR (CDCl_3 , 300 MHz) δ 3.36 (bs, 3H, $\text{NH}_2\&\text{OH}$), 4.66 (s, 2H, CH_2), 6.72 (q, $J=7.2$ Hz, 2H, Ar), 7.13 (m, 2H, Ar); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 64.31, 116.08, 118.22, 124.87, 129.17, 129.36, 145.94.; IR ($\nu_{\text{max}}/\text{cm}^{-1}$, neat) 3391, 2895, 1611, 1497, 1458, 1349, 1269, 1218, 1006, 752, 462.

RESULTS AND DISCUSSION

However, most catalysts in use today were discovered by trial and error, by "shaking and baking" metals and ceramics and then seeing how the results affect the reactions and their products [18]. As we enter the nano age, another approach appears. Indeed, nanotechnology, being defined as the creation of functional materials, devices, and systems through the control of matter at a scale of nanometers, as well as the exploitation of novel properties and phenomena developed on that scale [19].

So, in continuation of our research program directed to the application of nanotechnology as nano catalyst in organic reaction [20,21], we wish to introduce a novel and convenient method for one pot the reduction of various of aromatic carboxylic acids to the corresponding alcohols.

We first synthesis $\text{SiO}_2@\text{FeSO}_4$ nano catalyst by the sol - gel procedure and the size of the particles was observed by Scanning Electron Microscopy (SEM). The interaction of iron sulfate with the silica matrix in $\text{SiO}_2@\text{FeSO}_4$ nano catalyst has been investigated by IR-spectroscopy. The dimension of nanoparticles that was possible to observe is between 30-60 nm (Fig. 3). The results are in agreement with XRD data (Fig. 2).

Fig. 1 shows the IR spectra between 4000 and 400 cm^{-1} of the $\text{SiO}_2@\text{FeSO}_4$ nano catalyst. The spectra presented in Fig. 2 shows the main features attributed to Si-OH (970 cm^{-1}), Si-O-Si (1200 cm^{-1} and 1075 cm^{-1}), Fe-O (530 cm^{-1}), FeSO_4 (1178 cm^{-1}) as it was reported by other authors [22,23].

In order to optimize the reaction conditions, we performed reduction of benzoic acid as a model compound with sodium borohydride under different conditions. The effect of various molar ratios, solvent and reaction conditions were investigated in the typical experiment (Table 1). As seen, the combined system of benzoic acid with $\text{SiO}_2@\text{FeSO}_4$ nano catalyst in the absence of NaBH_4 and at reflux conditions was not effective and the reduction of benzoic acid with sodium borohydride in the absence of catalyst gives corresponding alcohol in poor yield and, however, the presence of nanoparticles in this reduction reaction improves the yield of primary alcohol significantly (Table 1).

The exact influence of $\text{SiO}_2@\text{FeSO}_4$ nano catalyst in the titled experiment is not clear; we think that by the immobilization of benzoic acid on $\text{SiO}_2@\text{FeSO}_4$ nano catalyst, the interaction of the C=O bond, NaBH_4 is increased. In addition, the results showed that 3 mmol of NaBH_4 in the presence of $\text{SiO}_2@\text{FeSO}_4$ nano catalyst (0.75 mmol) perfectly reduces one mmol of benzoic acid to benzylalcohol within 30 min. The reaction was carried out under solvent-free/oil bath condition with the simple reaction procedure and work-up (entry 1). We therefore selected these criteria as the optimum reaction conditions.

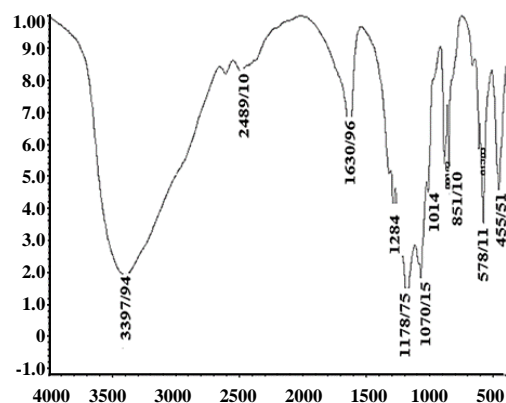


Fig. 1: FT-IR spectra of the synthesized $\text{SiO}_2@\text{FeSO}_4$ nanoparticles.

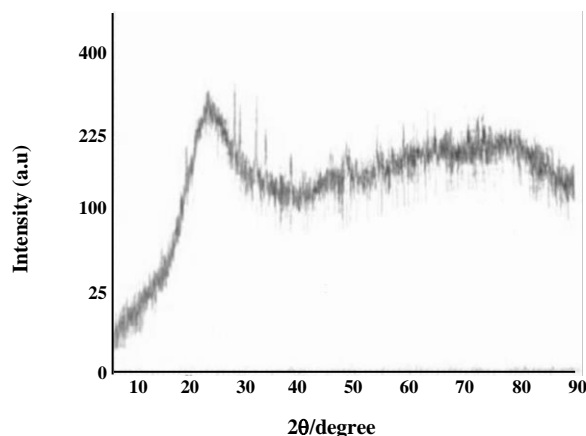


Fig. 2: XRD image of synthesis $\text{SiO}_2@\text{FeSO}_4$ nanoparticles.

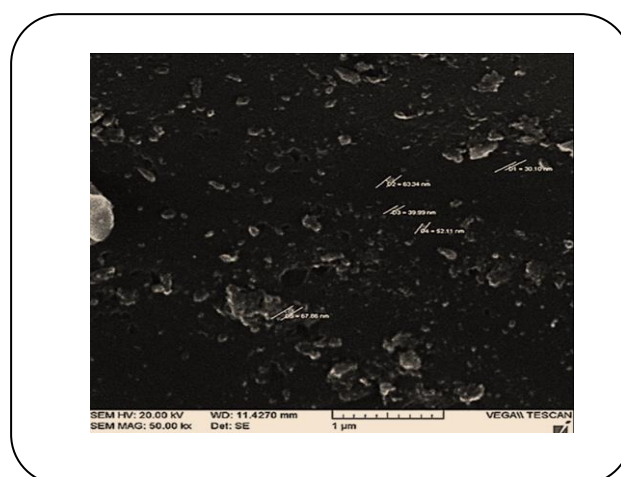


Fig. 3: SEM image of synthesis $\text{SiO}_2@\text{FeSO}_4$ nanoparticles.

Table 1: Optimization experiment for reduction of benzoic acid in $\text{SiO}_2@\text{FeSO}_4/\text{NaBH}_4$ system under different reaction conditions.

En	Component	Molar ratio	Condition ^{a,b}	Time (min)	Conversion (%) ^c
1	Sub./ $\text{SiO}_2@\text{FeSO}_4/\text{NaBH}_4$	1:0.5:3	Solvent-free/oil bath	60	80
2	Sub./ $\text{SiO}_2@\text{FeSO}_4/\text{NaBH}_4$	1:0.75:3	Solvent-free/oil bath	30	100
3	Sub./ $\text{SiO}_2@\text{FeSO}_4/\text{NaBH}_4$	1:1:3	Solvent-free/oil bath	30	100
4	Sub./ $\text{SiO}_2@\text{FeSO}_4/\text{NaBH}_4$	1:0.75:2	$\text{CH}_3\text{CN}/\text{reflux}$	60	25
5	Sub./ $\text{SiO}_2@\text{FeSO}_4/\text{NaBH}_4$	1:0.75:4	THF/reflux	55	30
6	Sub./ $\text{SiO}_2@\text{FeSO}_4/\text{NaBH}_4$	1:0.75:3	$\text{CH}_3\text{OH}/\text{reflux}$	60	15
7	Sub./ $\text{SiO}_2@\text{FeSO}_4$	1:1	Solvent-free/oil bath	60	-
8	Sub./ NaBH_4	1:4	Solvent-free/oil bath	60	2

a) Temperature of reflux was (70-80 °C).

b) Temperature of oil bath was (50-60 °C).

c) Monitored by thin layer chromatography (eluent; ethyl acetate: petroleum ether, 1:9).

The utility of the $\text{SiO}_2@\text{FeSO}_4/\text{NaBH}_4$ system was further studied by reduction of structurally different the carboxylic acid to the corresponding alcohol at the optimized conditions (Table 2). Reduction reactions were carried out under solvent-free/oil bath condition. All reactions were carried out successfully within 30-65 min to afford the alcohol in excellent yields.

A case study in Table 2 shows that aromatic acids containing nitro group were reduced completely to the corresponding amines under the experimental conditions. This means that the present protocol reduces nitro and acid functional groups with the same reactivity (Table 2, entries 2,3,4).

In addition, a comparison of the results in Table 2 shows that substrate containing electron withdrawing groups was reduced faster than substrate containing electron releasing groups under the same condition.

In this context, the regioselectivity of $\text{SiO}_2@\text{FeSO}_4/\text{NaBH}_4$ system in reduction of α,β -unsaturated carboxylic acid was examined by solvent-free reduction of cinnamyl acid with 3 molar equivalents of NaBH_4 in the presence of 0.75 molar equivalents of $\text{SiO}_2@\text{FeSO}_4$. The reaction was carried out efficiently and exclusively in 1,2-reduction manner in green reaction (solvent-free condition) (Table 2, entry 10).

In the next attempt, we turned our attention to recyclable of catalyst; the catalyst was separated by filtering from the reaction system and reused (after washing with distilled water/acetone and dried under *vacuum*) for four 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).

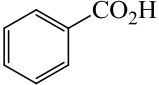
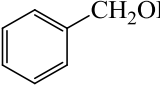
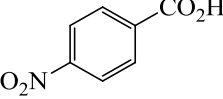
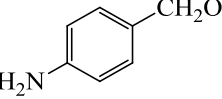
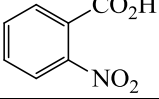
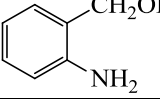
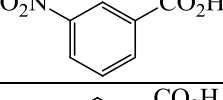
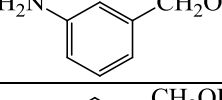
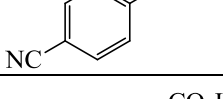
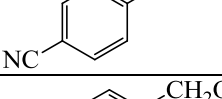
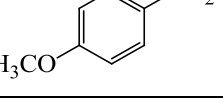
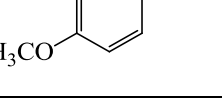
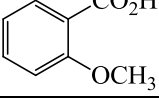
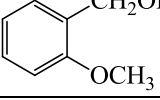
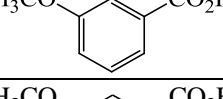
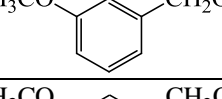
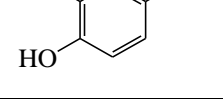
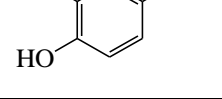
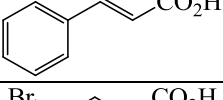
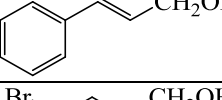
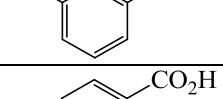
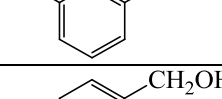
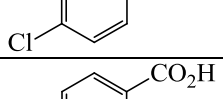
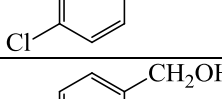
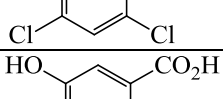
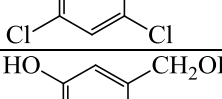
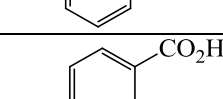
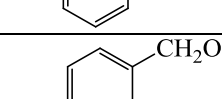
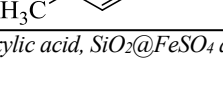
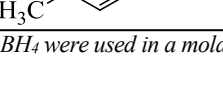
CONCLUSIONS

In summary, the application of sodium borohydride $\text{SiO}_2@\text{FeSO}_4$ nano catalyst system for reduction of carboxylic acids is illustrated by several examples involving important carboxylic acids. When compared to an aluminum hydride reduction, it proves to be an efficient and selective procedure which allows selective reduction of carboxylic acids in the presence of hydroxyl, amines, methoxy and heterocyclic functions.

Acknowledgments:

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Table 2: Reduction of Carboxylic Acids to Their Alcohols with $\text{SiO}_2@\text{FeSO}_4/\text{NaBH}_4$ system. ^a

En	Substrate	Product	Time (min)	Yield (%) ^b	Mp or bp °C/Torr (lit)[24]
1			30	90	202/760 (205.3/760)
2			30	92	62(59-63)
3			42	89	84(81-84)
4			32	93	94(91-95)
5			60	89	35(32-36)
6			50	90	26(22-25)
7			53	90	248/760 (248-250/760)
8			45	93	250/760 (252-254/760)
9			60	89	112(113)
10			65	85	32(30-32)
11			35	93	163/60 (165/760)
12			33	91	73(68-72)
13			40	90	58(57-60)
14			49	89	69(69-72)
15			55	90	61(59-61)

^a Carboxylic acid, $\text{SiO}_2@\text{FeSO}_4$ and NaBH_4 were used in a molar ratio of 1:0.75:3, respectively, ^b yields refer to isolated pure products.

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REFERENCES

- [1] Hu H., Xin J.H., Hu H., Wang X., Miao D., Liu Y., [Synthesis and Stabilization of Metal Nano Catalysts for Reduction Reactions – A Review](#), *J. Mater. Chem. A*, **3**: 11157-11182 (2015).
- [2] Kurtan U., Amir Md., Baykal A., [Fe₃O₄@Nico-Ag Magnetically Recyclable Nano Catalyst for Azo Dyes Reduction](#), *Appl. Surf. Sci.*, **363**: 66–73 (2016).
- [3] Aditya T., Pal A., Pal T., [Nitroarene Reduction: A Trusted Model Reaction to Test Nanoparticle Catalysts](#), *Chem. Commun.*, **51**: 9410-9431 (2015).
- [4] Shamsipur M., Bahrami Adeb N., Hajitarverdi M.S., Yazdimaghani M., Zarei F., [Influence of Micro and Nano Silica on Mechanical Properties of Plasticized Sulfur Composites](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **32**(3): 1-7 (2013).
- [5] Szostak M., Spain M., Procter D.J., [Electron Transfer Reduction of Carboxylic Acids Using SmI₂-H₂O-Et₃N](#), *Org. Lett.*, **14**(3): 840–843 (2012).
- [6] Stein Th.V., Meuresch M., Limper D., Schmitz M., Hölscher M., Coetzee J., Cole-Hamilton D.J., Klankermayer J., Leitner W., [Highly Versatile Catalytic Hydrogenation of Carboxylic and Carbonic Acid Derivatives using a Ru-Triphos Complex: Molecular Control over Selectivity and Substrate Scope](#), *J. Am. Chem. Soc.*, **136**(38):13217–13225 (2014).
- [7] Dub P.A., Ikariya T., [Catalytic Reductive Transformations of Carboxylic and Carbonic Acid Derivatives Using Molecular Hydrogen](#), *ACS Catal.*, **2**(8): 1718–1741 (2012).
- [8] Cha J.S., [Thirty Six Years of Research on the Selective Reduction and Hydroboration](#), *Bull. Korean Chem. Soc.*, **32**(6): 1808-1846 (2011).
- [9] Graetz J., Reilly J.J., Yartys V.A., Maehlen J.P., Bulychev B.M., Antonov V.E., Tarasov B.P., Gabis I.E., [Aluminum Hydride as A Hydrogen and Energy Storage Material: Past, Present and Future](#), *J. Alloys Compd.*, **509**: 517–528 (2011).
- [10] Bézier D., Park S., Brookhart M., [Selective Reduction of Carboxylic Acids to Aldehydes Catalyzed by B\(C₆F₅\)₃](#), *Org. Lett.*, **15**(3): 496–499 (2013).
- [11] Saavedra J.Z., Resendez A., Rovira A., Eagon S., Haddenham D., Singaram B., [Reaction of InCl₃ with Various Reducing Agents: InCl₃-NaBH₄-Mediated Reduction of Aromatic and Aliphatic Nitriles to Primary Amines](#), *J. Org. Chem.*, **77**(1): 221–228 (2012).
- [12] Banfi L., Narisano E., Riva R., Stiasni N., Hiersemann M., Yamada T., Tsubo T., [Sodium Borohydride](#), *E-EROS Encyclopedia of Reagents for Organic Synthesis*, 1–13(2014).
- [13] Pritchard J., Filonenko G.A., Putten R.V., Hensen E.J.M., Pidko E.A., [Heterogeneous and Homogeneous Catalysis for the Hydrogenation of Carboxylic Acid Derivatives: History, Advances and Future Directions](#), *Chem. Soc. Rev.*, **44**: 3808-3833 (2015).
- [14] Rao G.K., Gowda N.B., Ramakrishna R.A., [Raney Nickel-Catalyzed Hydrogenation of Unsaturated Carboxylic Acids with Sodium Borohydride in Water](#), *Synth. Commun.*, **42**(6): 893-904 (2012).
- [15] Jaita S., Kaewkum P., Duangkamol Ch., Phakhodee W., Pattarawarapan M., [Solvent-Free Reduction of Carboxylic Acids to Alcohols with NaBH₄ Promoted by 2,4,6-Trichloro-1,3,5-Triazine and PPh₃ in the Presence of K₂CO₃](#), *RSC Adv.*, **4**: 46947-46950 (2014).
- [16] Pulle J.S., Sagar A.D., Reddy S.R., Yadav M.V., [Reduction of Carboxylic Acids to Alcohols Using Phosphonitrilic Chloride and Sodium Borohydride](#), *Der Chemica Sinica*, **6**(5): 104-107 (2015).
- [17] Karimkoshteh M., Bagheri M., Zeynizadeh B., [SiO₂@FeSO₄ Nano Composite: a Recoverable Nano-Catalyst for Eco-Friendly Synthesis Oximes of Carbonyl Compounds](#), *Nano. Chem. Res.*, **1**(1): 57-63 (2016).
- [18] Saberi D., Mansoori S., Ghaderi E., Niknam Kh., [Copper Nanoparticles on Charcoal: an Effective Nanocatalyst for the Synthesis of Enol Carbamates and Amides Via an Oxidative Coupling Route](#), *Tetrahedron Lett.*, **57**: 95–99 (2016).
- [19] Vissers D.R., Isheim D., Zhan Ch., Chen Z., Lu J., Amine Kh., [Understanding Atomic Scale Phenomena Within the Surface Layer of a Long-Term Cycled 5 V Spinel Electrode](#), *Nano Energy*, **19**: 297–306 (2016).

- [20] Karimkoshteh M., Zeynizadeh B., Bagheri M., [Selective Method for Reduction of Oximes to Amines in the Presence of Cu Nanoparticle](#), *Iran. J. Sci. Technol. A.*, **39A**: 527-532 (2015).
- [21] Karimkoshteh M., Bagheri M., Zeynizadeh B., [SiO₂@FeSO₄ Nano Composite as Nanocatalyst for the Green Synthesis 1,1-Diacetates from Aldehydes Under Solvent-Free Conditions](#), *J. Chil. Chem. Soc.*, **61**: 2780-2783 (2016).
- [22] Tohidi S.H., Grigoryan G., Sarkeziyan V., Ziaie F., [Effect of Concentration and Thermal Treatment on the Properties of Sol-Gel Derived CuO/SiO₂ Nanostructure](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **29**(2): 27-35 (2010).
- [23] Wang J., Zheng Sh., Shao Y., Liu J., Xu Zh., Zhu D., [Amino-Functionalized Fe₃O₄@SiO₂ Core-Shell Magnetic Nanomaterial as a Novel Adsorbent for Aqueous Heavy Metals Removal](#), *J. Colloid Interface Sci.*, **349**(1): 293-299 (2010).
- [24] Haynes W.M., " [CRC Handbook of Chemistry and Physics](#)", 96th Ed., Taylor & Francis Group, Abingdon, (2016).