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Ionic liquid immobilized on $FeNi_3$ as catalysts for efficient, green, and one-pot synthesis of 1,3-thiazolidin-4-one

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ABSTRACT

A magnetically ionic liquid (ILs) supported on $FeNi_3$ nanocatalyst was synthesized and evaluated as a recoverable catalyst for the synthesis of 1,3-thiazolidin-4-one. The main targets are solvent-free conditions, rapid (immediately) and easy immobilization technique, and low cost precursors for the preparation of highly active and stable MPs with high densities of functional groups. The inorganic, magnetic, solid base catalyst was characterized via Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). The catalyst is active for the synthesis of 1,3-thiazolidin-4-ones and the products are isolated in high to excellent yields. Supporting this base catalyst on magnetic particles offers a simple and non-energy-intensive method for recovery and reuse of the catalyst by applying an external magnet. Isolated catalysts were reused for new rounds of reactions without significant loss of their catalytic activity.

1. Introduction

The thiazolidin-4-one ring system is a core structure found in various synthetic pharmaceutical compounds, displaying a broad spectrum of biological activities [1–6]. Consequently, several synthetic methods have been developed for the synthesis of 4-thiazolidinones. The main synthetic routes to thiazolidin-4-ones involve cyclo-condensation of azomethines (Schiff's base) with mercaptoacetic acid [7]. There are also reports using chemical agents, such as N-methylpyridinium tosylate [8] as desiccant, to assist the formation of thiazolidinone derivatives. The use of [BmIm]OH [9], Hunig's base [10], and Baker's yeast [11] has also been reported to expedite the cyclo-condensation of the azomethines and thioglycolic acid.

Ionic liquids (ILs) have emerged as promising homogeneous catalysts [12] because of their unique physicochemical properties including negligible vapor pressure, wide liquid range, high ionic conductivity and excellent solubility [13]. Although ILs possess some advantages but their practical applications have been restricted by some difficulties in its recovery which lead to economical and environmental problems. On the other hand, their high viscosity not only limits their mass transfer during catalytic reactions but also makes their handling difficult. Moreover, the use of relatively large amounts of ILs is costly and may cause toxicological concerns. These problems can be overcome by immobilization of ILs onto solid supports to obtain heterogeneous catalysts [14–16].

In recent years, core–shell multi-components have attracted intense attention because of their potential applications in catalysis [17]. Different from single-component that can only supply people with one function, the core–shell multi-components can integrate multiple functions into one system for specific applications [18–22]. Moreover, the interactions between different components can greatly improve the performance of the multi-components system and even generate new synergetic properties. Among the core–shell structured composites, the composites with magnetic core and functional shell structures have received especial attention because of their potential applications in catalysis, drug storage/release, selective separation, chromatography, and chemical or biologic sensors [23–32]. The magnetic core has good magnetic responsibility, and can be easily magnetized. Therefore, the composites with magnetic core can be conveniently collected, separated or fixed by external magnet. Engaged in the development of greener and sustainable pathways for organic transformations, nanomaterial, and nano-catalysis [33–36], herein, we report a simple and efficient synthesis of a nano-ferrite-supported, magnetically recyclable, and inexpensive ionic liquids catalyst and its application for the synthesis 1,3-thiazolidin-4-ones (Scheme 1).

2. Experimental

2.1. Materials and methods

Chemical materials were purchased from Fluka and Merck in high purity. Melting points were determined in open capillaries using an

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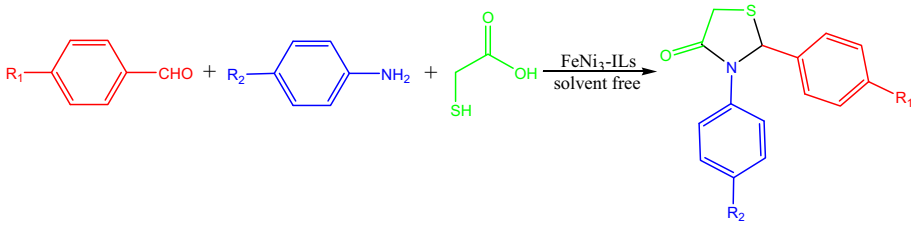

Scheme 1. Synthesis of thiazolidinon-4-ones in the presence of $FeNi_3$-ionic liquids MNPs.

Electrothermal 9100 apparatus are uncorrected. FTIR spectra were recorded on a VERTEX 70 spectrometer (Bruker) in the transmission mode in spectroscopic grade KBr pellets for all the powders. The particle size and structure were observed by using a Philips CM10 transmission electron microscope operating at 100 KV. Powder X-ray diffraction data was obtained using Bruker D8 Advance model with Cu ka radition. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA449F3 at a heating rate of 10 °C min^{-1} under nitrogen. The magnetic measurement was carried out in a vibrating sample magnetometer (VSM) (4 inch, Daghigh Meghnatis Kashan Co., Kashan, Iran) at room temperature. NMR spectra were recorded in DMSO on a Bruker Avance DRX-400 MHz instrument spectrometer using TMS as internal standard. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates.

2.2. General procedure for the preparation of $FeNi_3$ nanoparticles

$FeCl_2 \cdot 4H_2O$ (1.72 g) and $NiCl_2 \cdot 6H_2O$ (4.72 g) were dissolved in 80 mL of deaerated highly purified water contained in a three neck flask with vigorous stirring (800 rpm) under nitrogen. As the temperature was elevated to 80 °C, 10 mL of ammonium hydroxide was added drop by drop, and the reaction was maintained for 30 min. hydrazine hydrate (20 mL, 80% concentration) was added to the above suspension. The black product was separated by putting the vessel on a permanent magnet and the supernatant was decanted. The black precipitate was washed for six times with highly purified water to remove the unreacted chemicals, then the black product $FeNi_3$ was dried in the vacuum.

2.3. General procedure for the preparation of $FeNi_3/SiO_2$ nanoparticles

Firstly, a mixture of ethanol (100 mL) and distilled water (20 mL) was added to magnetic nanoparticles (1 g), and the resulting dispersion was sonicated for 10 min. After adding ammonia water (2.5 mL), tetraethyl orthosilicate (TEOS, 2 mL) was added to the reaction solution. The resulting dispersion was under mechanically stirred continuously for 20 h at room temperature. The magnetic $FeNi_3/SiO_2$ nanoparticles were collected by magnetic separation and washed with ethanol and deionized water in sequence.

2.4. General procedure for the preparation of $FeNi_3/SiO_2/SO_3H$ nanoparticles

To a round-bottomed flask (100 mL) $FeNi_3/SiO_2$ MNPs (0.40 g) in CH_2Cl_2 (50 mL), was added chlorosulfonic acid (12 mmol) dropwise over a period of 20 min at room temperature (Fig. 1). After vigorous stirring for 24 h, the magnetic $FeNi_3/SiO_2/SO_3H$ nanoparticles were collected by magnetic separation and washed with ethanol and deionized water in sequence.

2.5. General procedure for the preparation of $FeNi_3$-ILs nanoparticles

Ethanolamine (5 mmol) was dispersed in dry CH_2Cl_2 (20 mL) and $FeNi_3/SiO_2/SO_3H$ (0.1 g) nanoparticles were added. Then the mixture was heated to 60 °C for 12 h under nitrogen atmosphere. The resulting solid was separated by an external magnet and washed 3 times with CH_2Cl_2, ethanol and H_2O. After drying at room temperature in vacuum, $FeNi_3$-ILs were obtained as reddish-brown powder.

2.6. General procedures for preparation of 1,3-thiazolidin-4-ones

A mixture of aldehyde (1 mmol), amine (1 mmol), thioglycolic acid (1 mmol), and $FeNi_3$-ILs MNPs (0.001 g) was stirred at 50 °C. Upon completion, the progress of the reaction was monitored by TLC when the reaction was completed, EtOH was added to the reaction mixture and the $FeNi_3$-ILs MNPs was separated by external magnet. Then the solvent was removed from solution under reduced pressure and the resulting product purified by recrystallization using *n*-hexane/ethyl acetate.

2.7. Selected spectral data of the products 2-(2-nitrophenyl)-3-p-tolylthiazolidin-4-one (4c)

IR (KBr): υ = 3036, 2930, 1723, 1548, 1529, 1352 cm^{-1}; ^1H NMR (400 MHz, DMSO-*d6*): υ = 8.01 (d, *J* = 8.1 Hz, 1H.), 7.70–7.73 (m, 2H), 7.47–7.52 (m, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.72 (s, 1H), 3.98 (d, *J* = 15.7 Hz, 1H), 3.78 (d, *J* = 15.8 Hz, 1H), 2.18 (s, 3H) ppm.

3. Results and discussion

We report the synthesis of a magnetic particle-based solid base with a high density of ionic liquids groups and discuss its performance as a novel strong and stable magnetic ionic liquid. We were intrigued by

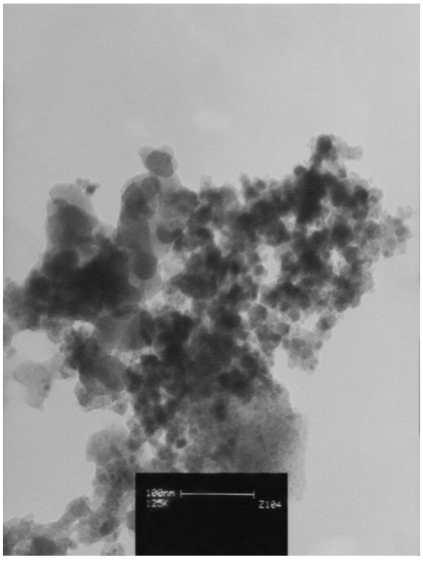

Fig. 1. (a) TEM images of $FeNi_3$-ILs MNPs.

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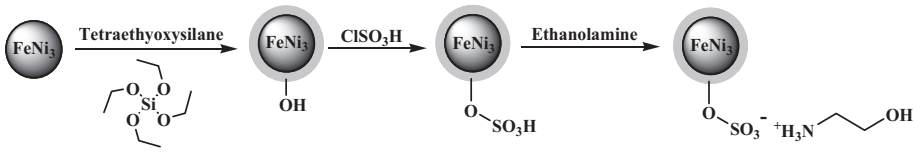


Scheme 2. Schematic illustration of the synthesis for $FeNi_3$-ILs MNPs.

the possibility of applying ionic liquid and nanotechnology for the design of a novel, active, recyclable, and magnetically recoverable ionic liquid base derivative (Scheme 2).

The size and structure of the $FeNi_3$-ILs MNPs were also evaluated using transmission electron microscopy (TEM) (Fig. 1). After being coated with a SiO_2 and organic layer, the typical core–shell structure of the $FeNi_3$-ILs MNPs can be observed. The dispersity of $FeNi_3$-ILs MNPs is also improved, and the average size increases to about 20–30 nm.

The structural properties of synthesized $FeNi_3$-ILs MNPs were analyzed by X-ray power diffraction (XRD). As shown in Fig. 2, XRD patterns of the synthesized $FeNi_3$-ILs MNPs display several relatively strong reflection peaks in the 2θ region of 20–80°, which is quite similar to those of $FeNi_3$ nanoparticles reported by other group. It can be seen that three characteristic peaks for (FCC)-$FeNi_3$ ($2\theta = 44.3°$, 51.5°, 75.9°) from (111), (200), and (220) planes, are obtained. The sharp and strong diffraction peaks confirm the good crystallization of the products (Fig. 2a). The broad band at $2\theta = 15.0°–30.0°$ can be assigned to the amorphous SiO_2 shell (Fig. 2b) (JCPDS card No. 29-0085).

This structure was further supported by the FT-IR spectra. The FT-IR spectrum of $FeNi_3$-ILs MNPs showed the typical bands at 2921 and 2866 cm^{-1} attributed to C–H stretching vibrations of alkyl chains. Moreover, the broad peak at 1033 cm^{-1} belonged to S═O stretching vibrations in the sulphonate functional groups. Bands at 1624 and 1502 cm^{-1} were related to N–H bending vibrations in the ammonium groups. These results indicated that IL was successfully immobilized on $FeNi_3$ MNPs (Fig. 2c).

The thermal behavior of $FeNi_3$-ILs MNPs is shown in Fig. 2d. A significant decrease in the weight percentage of the $FeNi_3$-ILs MNPs at about 130 °C is related to desorption of water molecules from the catalyst surface. This was evaluated to be 1–3% according to the TG analysis. In addition, the analysis showed two other decreasing peaks. The first peak appears at temperature around 250–280 °C due to the decomposition of SO_3H. This is followed by a second peak at 420–460 °C, corresponding to the loss of the organic spacer group. According to the TGA, the amount of IL supported on $FeNi_3/SiO_2$ was evaluated to be 0.15 mmol g^{-1}. The loading amount of IL on $FeNi_3/SiO_2$ was also quantified *via* elemental analysis and it was 0.15 mmol g^{-1} based on nitrogen and sulfur determination (0.21% and 0.48%, respectively).

The magnetic properties of the nanoparticles were characterized using a vibrating sample magnetometer (VSM). The magnetization curves of the obtained nanocomposite registered at 300 K show that nearly no residual magnetism is detected (Fig. 3), which means that the nanocomposite exhibited the paramagnetic characteristics. Magnetic

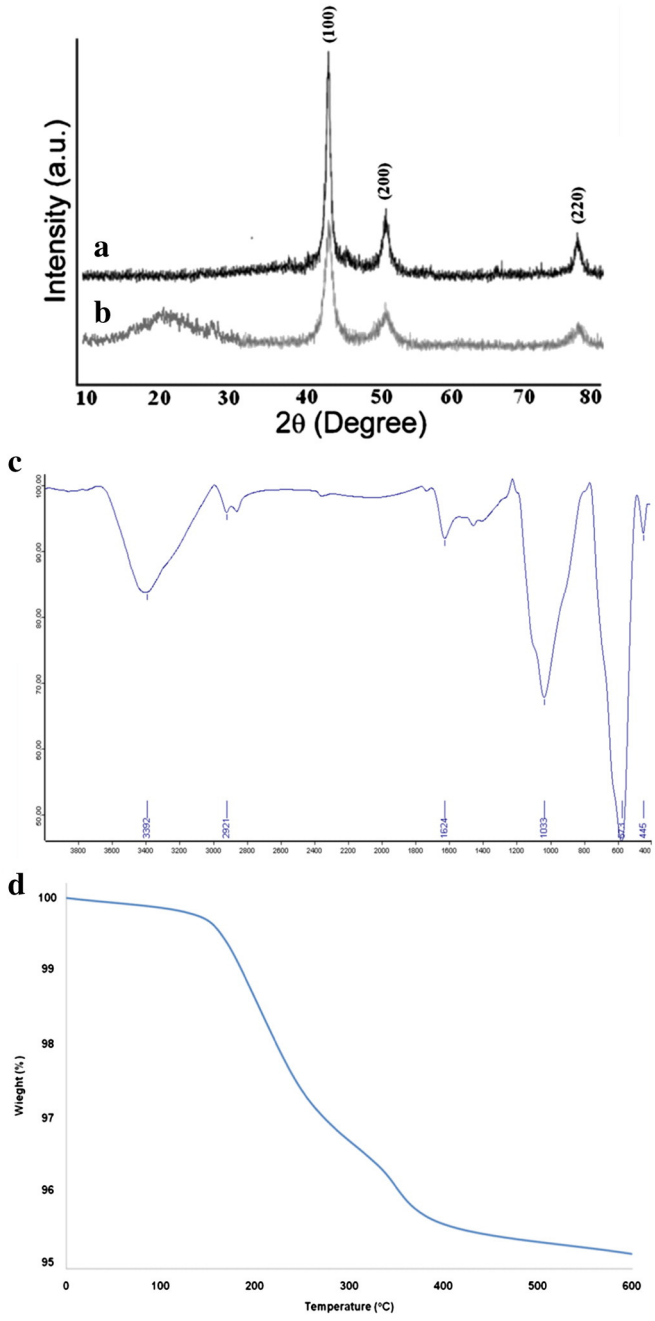


Fig. 2. XRD analysis of (a) $FeNi_3$ MNPs and (b) $FeNi_3$-ILs MNPs, (c) FTIR spectra of $FeNi_3$-ILs MNPs, and (d) TGA diagram of $FeNi_3$-ILs MNPs.

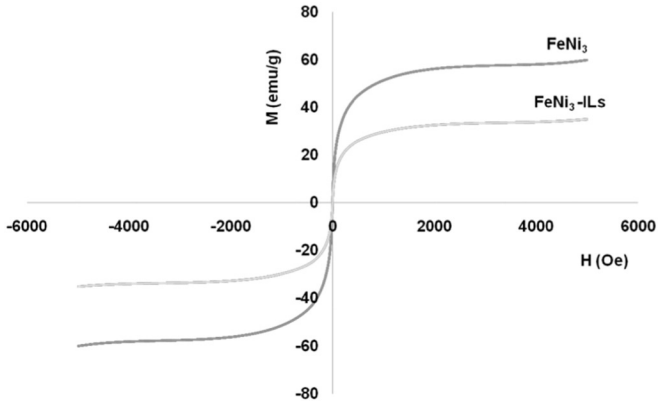


Fig. 3. Room-temperature magnetization curves of the nano catalysis.

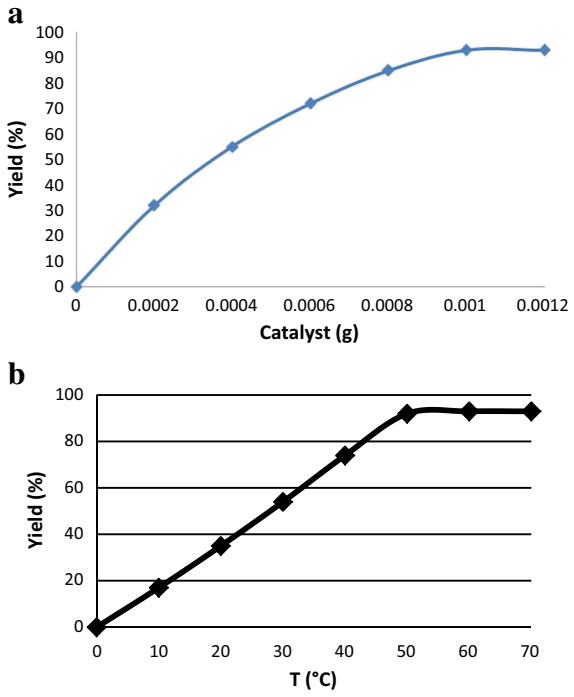
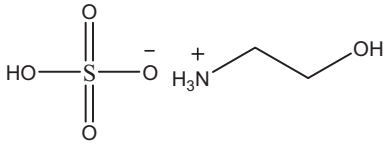


Fig. 4. (a) Effect of increasing amount of $FeNi_3$-ILs MNPs on the preparation of 1,3-thiazolidin-4-one in the presence of $FeNi_3$-ILs MNPs at 100 (°C); (b) reaction progress monitored by GC.

measurement shows that pure $FeNi_3$, and $FeNi_3$-ILs have saturation magnetization values of 55.2, and 30.4 emu/g respectively. These nanocomposites with paramagnetic characteristics and high magnetization values can quickly respond to the external magnetic field and quickly redisperse once the external magnetic field is removed. The result reveals that the nanocomposite exhibits good magnetic responsible, which suggests a potential application for targeting and separation.

Under the optimal conditions, the same reaction was carried out in various solvents under similar conditions. In this study, it was found that a solvent-free condition is more efficient over other solvents with respect to reaction time and yield of the desired 1,3-thiazolidin-4-one. Then the reaction progress in the presence of 0.001 g of $FeNi_3$-ILs MNPs was monitored by GC (Fig. 4a). Using this catalyst system, excellent yields of 1,3-thiazolidin-4-one can be achieved in 1 h at 50 °C. No apparent by-products were observed by GC in all the experiments and the cyclic carbonate was obtained cleanly in 93% yield (Fig. 4b).

The catalytic activity of the $FeNi_3$-ILs MNPs was compared with the ILs (Scheme 3). For this purpose, the reactions were carried out separately at 50 °C with both the catalysts for the appropriate time (Table 1). The aliquots of the reaction mixture were collected periodically at an interval of 20 min. Table 1 shows the variation of the percentage preparation of 1,3-thiazolidin-4-one with time, when $FeNi_3$-ILs MNPs and ILs were employed as catalysts. It is evident that, the catalytic activity of the $FeNi_3$-ILs MNPs is similar with the ILs. After 60 min $FeNi_3$-ILs MNPs showed 93% preparation of 1,3-thiazolidin-4-one as compared to 88% with ILs. After 100 min yield of the product in the presence of $FeNi_3$-ILs



Scheme 3. Image of ILs.

Table 1
Comparative of the catalytic activity of $FeNi_3$-ILs MNPs with ILs.[a]

Entry	Reaction time (min)	Yield (%)[b]	
		$FeNi_3$-ILs	ILs
1	20	64	61
2	40	70	68
3	60	93	88
4	80	93	92
5	100	93	94

[a] Reaction condition: aldehyde (1 mmol), amine (1 mmol), thioglycolic acid (1 mmol), and $FeNi_3$-ILs MNPs or ILs (1 mol.%) at 50 °C.
[b] Isolated yields.

MNPs is fixed in 93% but ILs showed 94% preparation of product. The nano-sized particles increase the exposed surface area of the active component of the catalyst, thereby enhancing the contact between reactants and catalyst dramatically and mimicking the homogeneous catalysts. Also, the activity and selectivity of nano-catalyst can be manipulated by tailoring chemical and physical properties like size, shape, composition and morphology.

After optimization of the reaction conditions, to delineate this approach, particularly in regard to library construction, this methodology was evaluated by using different amines, variety of different substituted aldehyde and of thioglycolic acid in the presence of $FeNi_3$-ILs MNPs under similar conditions. As can be seen from (Table 2), electronic effects and the nature of substituents on the amines and aldehyde did not show strongly obvious effects in terms of yields under the reaction conditions. The three-component cyclocondensation reaction proceeded smoothly.

A mechanism for the reaction is outlined in Scheme 4. The reaction occurs via initial formation of the imine intermediate [A] from the condensation of aldehyde and amine, which reacts with thioglycolic acid to give the intermediate which subsequently cyclises to afford the desired 1,3-thiazolidin-4-one. The nano-PbS has Lewis acid (NH_3^+) and Lewis basic (OH^-) sites.

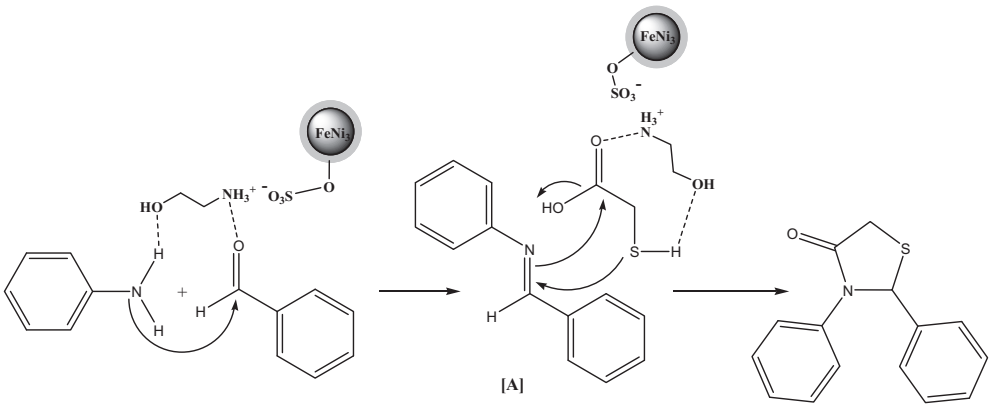
4. Conclusion

In summary, $FeNi_3$-ILs MNP as a new magnetic nanoparticle catalyst was synthesized directly through reaction of chlorosulfonic acid and ethanolamine supported on $FeNi_3/SiO_2$ MNPs. The synthesized $FeNi_3$-IL MNP was used as a magnetically recyclable heterogeneous catalyst for the efficient one-pot synthesis of 1,3-thiazolidin-4-one from the reaction of aldehyde, amine, and thioglycolic acid with high product yields. The catalytic research on novel approaches toward nanomaterials should be improved to enhance organic synthesis. For that purpose, nanoparticle catalyst provides a new way for continuous processes, because of its simple recyclability. From a scientific point, our results

Table 2
Synthesis of 1,3-thiazolidin-4-one derivatives catalyzed by $FeNi_3$-ILs MNPs.[a]

Entry	R_1	R_2	Product	Yield (%)[b]	Mp
1	Me	Me	4a	93	121–123 [37]
2	H	Me	4b	90	105–107 [37]
3	NO_2	Me	4c	89	157–159
4	H	H	4d	91	129–131 [37]
5	Cl	H	4e	94	122–124 [37]
6	Me	H	4f	86	116–118 [37]
7	NO_2	H	4g	92	105–107 [37]
8	H	Cl	4h	90	121–123 [37]
9	H	NO_2	4i	90	160–162 [37]

[a] Reaction condition: aldehyde (1 mmol), amine (1 mmol), thioglycolic acid (1 mmol), and $FeNi_3$-ILs MNPs (0.001 g) at 50 °C.
[b] Yield refers to isolated product.



Scheme 4. A possible mechanism for the one-pot reaction for the synthesis 1,3-thiazolidin-4-one.

expand the application of nanoparticles. This catalyst should be helpful to development of new catalytic systems.

References

[1] Y.X. Li, X. Zhai, W.K. Liao, Chin. Chem. Lett. 23 (2012) 415–418.
[2] D. Bhambi, V.K. Salvi, J.L. Jat, S. Ojha, G.L. Talesara, J. Sulfur Chem. 28 (2007) 155–163.
[3] X. Zhang, X. Li, D. Li, Bioorg. Med. Chem. Lett. 19 (2009) 6280–6283.
[4] A. Mobinikhaledi, N. Foroughifar, M. Kalhor, J. Heterocycl. Chem. 47 (2010) 77–80.
[5] X. Jin, C.J. Zheng, M.X. Song, Eur. Med. Chem. 56 (2012) 203–209.
[6] X.J. Sun, W.L. Dong, W.G. Zhao, Z.M. Li, Chin. J. Org. Chem. 27 (2007) 1374–1380.
[7] B. Chandrasekhar, J. Sulfur Chem. 29 (2008) 187–240.
[8] D. Gautam, P. Gautam, R.P. Chaudhary, Chin. Chem. Lett. 23 (2012) 1221–1224.
[9] S.G. Patil, R.R. Bagul, M.S. Swami, Chin. Chem. Lett. 22 (2011) 883–886.
[10] V. Gududuru, V. Nguyen, J.T. Dalton, D.D. Miller, Synlett (2004) 2357–2358.
[11] U.R. Pratap, D.V. Jawale, M.R. Bhosle, R.A. Mane, Tetrahedron Lett. 52 (2011) 1689–1691.
[12] P.J. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772–3789.
[13] T. Welton, Chem. Rev. 99 (1999) 2071–2084.
[14] T. Selvam, A. Machoke, W. Schwieger, Appl. Catal. A Gen. 445–446 (2012) 92–101.
[15] Y.H. Kim, S. Shin, H.J. Yoon, J.W. Kim, J.K. Cho, Y.S. Lee, Catal. Commun. 40 (2013) 18–22.
[16] J. Miao, H. Wan, Y. Shao, G. Guan, B. Xu, J. Mol. Catal. A: Chem. 348 (2011) 77–82.
[17] C.L. Zhu, M.L. Zhang, Y.J. Qiao, G. Xiao, F. Zhang, J. Phys. Chem. C 114 (2010) 16229–16235.
[18] J.Q. Hu, Y. Bando, J.H. Zhan, D. Golberg, Appl. Phys. Lett. 85 (2004) 3593–3595.
[19] B. Liu, H.C. Zeng, Small 1 (2005) 566–571.
[20] J. Cao, J.Z. Sun, J. Hong, H.Y. Li, H.Z. Chen, M. Wang, Adv. Mater. 16 (2004) 84–87.
[21] X.M. Sun, Y.D. Li, Angew. Chem. Int. Ed. 43 (2004) 597–601.
[22] Q.B. Wang, Y. Liu, Y.G. Ke, H. Yan, Angew. Chem. Int. Ed. 47 (2008) 316–319.
[23] J.L. Lyon, D.A. Fleming, M.B. Stone, P. Schiffer, M.E. Williams, Nano Lett. 4 (2004) 719–723.
[24] P.P. Yang, Z.W. Quan, Z.Y. Hou, C.X. Li, X.J. Kang, Z.Y. Cheng, J. Lin, Biomaterials 30 (2009) 4786–4795.
[25] M. Zhang, Y.P. Wu, X.Z. Feng, X.W. He, L.X. Chen, Y.K. Zhang, J. Mater. Chem. 20 (2010) 5835–5842.
[26] S.S. Liu, H.M. Chen, X.H. Lu, C.H. Deng, X.M. Zhang, P.Y. Yang, Angew. Chem. Int. Ed. 49 (2010) 7557–7561.
[27] Y.H. Won, D. Aboagye, H.S. Jang, A. Jitianu, L.A. Stanciu, J. Mater. Chem. 20 (2010) 5030–5034.
[28] Y. Li, J.S. Wu, D.W. Qi, X.Q. Xu, C.H. Deng, P.Y. Yang, X.M. Zhuang, Chem. Commun. (2008) 564–566.
[29] J. Deng, L.P. Mo, F.Y. Zhao, L.L. Hou, L. Yang, Z.H. Zhang, Green Chem. 13 (2011) 2576–2584.
[30] Y.H. Liu, J. Deng, J.W. Gao, Z.H. Zhang, Adv. Synth. Catal. 354 (2012) 441–447.
[31] P.H. Li, B.L. Li, Z.M. An, L.P. Mo, Z.S. Cui, Z.H. Zhang, Adv. Synth. Catal. 355 (2013) 2952–2959.
[32] F.P. Ma, P.H. Li, B.L. Li, L.P. Mo, N. Liu, H.J. Kang, Y.N. Liu, Z.H. Zhang, Appl. Catal. A Gen. 457 (2013) 34–41.
[33] M.A. Nasseri, S.M. Sadeghzadeh, J. Iran. Chem. Soc. 10 (2013) 1047–1056.
[34] M.A. Nasseri, S.M. Sadeghzadeh, J. Chem. Sci. 125 (2013) 537–544.
[35] M.A. Nasseri, S.M. Sadeghzadeh, Monatsh. Chem. 144 (2013) 1551–1558.
[36] S.M. Sadeghzadeh, M.A. Nasseri, Catal. Today 217 (2013) 80–85.
[37] A. Bolognese, G. Correale, M. Manfra, Org. Biomol. Chem. 2 (2004) 2809–2813.