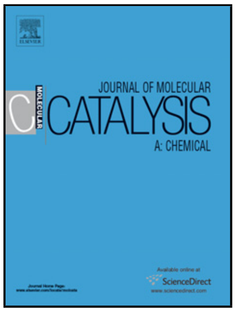


Title: Synthesis, characterization and catalytic application of a novel polyethylene-supported Fe/ionic liquid complex

Author: Davar Elhamifar Dawood Elhamifar Frood Shojaeipoor

PII: S1381-1169(16)30489-7
DOI: http://dx.doi.org/doi:10.1016/j.molcata.2016.11.015
Reference: MOLCAA 10112

To appear in: *Journal of Molecular Catalysis A: Chemical*

Received date: 12-5-2016
Revised date: 18-10-2016
Accepted date: 8-11-2016

Please cite this article as: Davar Elhamifar, Dawood Elhamifar, Frood Shojaeipoor, Synthesis, characterization and catalytic application of a novel polyethylene-supported Fe/ionic liquid complex, Journal of Molecular Catalysis A: Chemical http://dx.doi.org/10.1016/j.molcata.2016.11.015

Synthesis, characterization and catalytic application of a novel polyethylene-supported Fe/ionic liquid complex

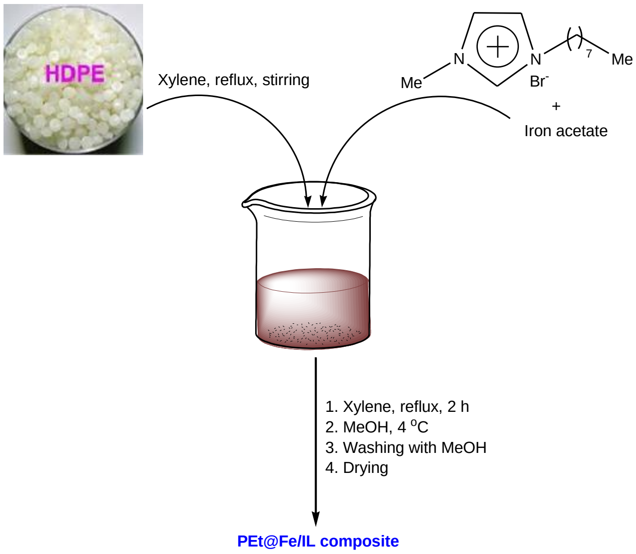
Davar Elhamifar,[a,b] Dawood Elhamifar[c,*] and Frood Shojaeipoor[d]

[a]Department of Chemical Engineering, Islamic Azad University, Shahreza Branch, Isfahan, Iran
[b]Mehr Petrochemical Company, Phase 2 of PSEEZ, Assaluyeh, Bushehr, Iran
[c]Department of Chemistry, Yasouj University, Yasouj, 7518-74831, Iran
[d]Department of Chemistry, Payame Noor University, Tehran, 19395-4697, Iran

[*] *To whom correspondence should be addressed. Tel&fax. (0098)-743-3233977, E-mail: d.elhamifar@yu.ac.ir*

Graphical abstract

A novel polyethylene-supported ionic liquid/iron complex is prepared, characterized and its catalytic application is developed in the synthesis of 3,4-dihydropyrimidinones through Biginelli reaction. The corresponding coupling products were obtained in high to excellent yield and selectivity. Moreover, the catalyst was recovered and reused several times without decrease in efficiency.



Highlights

- For the first time, a novel polyethylene-supported ionic liquid/iron complex (PEt@Fe/IL) is prepared and characterized
- The chemical properties and thermal stability of the PEt@Fe/IL was investigated using DRIFTs, EDX, TGA, XPS and SEM
- The PEt@Fe/IL was successfully applied in the one-pot Biginelli condensation of aldehydes, urea and alkylacetoacetates
- The coupling products were obtained in high to excellent yield and selectivity
- The PEt@Fe/IL was recovered and reused several times without significant decrease in efficiency

Abstract

A novel polyethylene-supported Fe/ionic liquid complex (PEt@Fe/IL) is prepared, characterized and its catalytic performance is investigated in the synthesis of 3,4-dihydropyrimidinones. The chemical properties and thermal stability of the PEt@Fe/IL material were studied by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, thermal gravimetric analysis (TGA) and energy dispersive X-ray (EDAX) analysis. The morphology of the material was obtained using scanning electron microscopy (SEM). The PEt@Fe/IL material was then successfully applied in the Biginelli condensation of aldehydes, urea and alkylacetoacetates to prepare a set of different 3,4-dihydropyrimidinone derivatives in high to excellent yields. The PEt@Fe/IL was recovered and reused several times without significant decrease in efficiency. The other advantages of this novel catalytic system include excellent yield, short reaction time and solvent-free conditions.

Keywords: Polymer-supported catalyst, Fe/ionic liquid complex; 3,4-dihydropyrimidinones; solvent free conditions, recoverable and reusable catalyst

1. Introduction

One pot synthesis of 3,4-dihydropyrimidine-2-(1H)-ones through Biginelli reaction is an important chemical process due to its key role in the preparation of biologically useful compounds. This reaction involves three component cyclocondensation of alkyl-acetoacetates, aldehydes and urea/thiourea under acidic conditions [1-2]. Some promising biological effects of the 3,4-dihydropyrimidine-2-(1H)-ones include antiviral, antibacterial, antitumor, and anti-inflammatory activities. They have also been found to be as calcium channel modulators [3], antihypertensive agents [4] and α-1a-antagonists [5]. According to aforementioned advantages of the Biginelli products, to date many synthetic protocols for preparing these compounds have been reported in the presence of both Lewis and Brønsted acid catalysts under homogeneous conditions [6-10]. However, the problems of catalyst and product separation, catalyst recovery and also environmental pollution have restricted these catalytic systems. To overcome these limitations, the immobilization of homogeneous catalysts onto/into solid supports has been recently developed [11, 12]. Along this line, more recently we also have prepared a number of ionic liquid based nano-organosilicas supported acid catalysts and studied their application in the Biginelli condensations [13, 14].

On the other hand, metal–polymer composites exhibiting the properties of both metals and polymers have been the subject of research interest at last two decades. Structure and properties of these composites are very important to design new engineering materials with desired characteristics [15]. In fact, to improve properties such as thermal and electrical conductivity, mechanical stability, chemical reactivity, and to stiffen the matrix, various kinds of fillers and additives such as metal or ceramic are introduced into polymer matrix [15-18]. The properties of the composite materials depend on the volume fraction of the fillers and additives as well as the interfacial compatibility between the additives and the matrix [19]. Various kinds of polymers and polymer matrix composites reinforced with metal particles have a wide range of industrial applications such as heaters and electrodes [20]. Non-toxic and environmentally bearable metals have widely been tested as a viable alternative to other more expensive metal-containing polymeric catalysts [21]. For example, catalysts containing metals such as scandium, molybdenum, copper, nickel, manganese, and others have been successfully employed [22-26]. Catalysts based on one of the earth most abundant and cheapest metal, iron, have been also tested to overcome safety, ecological and toxicity drawbacks associated with toxic metals [27,28]. But the search still continues for more active iron-based catalysts able to operate under more sustainable conditions. Moreover, the incorporation and immobilization of ionic liquids into the polymer systems has been an interesting topic because ionic liquids can be used as solvents, processing aides and plasticizers to enhance the polymer properties [29-31]. According to these and in continuous studies in the Biginelli reaction, in the present work a novel Fe/ionic liquid complex containing polyethylene (PEt@Fe/IL, Scheme 1) is prepared, characterized and its catalytic performance is investigated in the synthesis of 3,4-dihydropyrimidinones through Biginelli reaction. Our study showed that the

PEt@Fe/IL was very effective and could be recovered and reused several times without significant decrease in its efficiency.

2. Experimental

2.1. Preparation of methyl-octyl-imidazolium bromide/Fe (Fe/IL) complex

Firstly, N-methyl-imidazole (5 mmol) and octyl-bromide (5 mmol) were added in toluene and refluxed with stirring for 36 h. After cooling reaction temperature to room temperature, a biphasic system (including ionic liquid and toluene phases) was obtained. The supernatant toluene solution was next removed and the ionic liquid phase was washed several times with toluene to remove impurities. After removing solvent and drying at 70 °C, a viscous liquid called methyl-octyl-imidazolium bromide ([MOIM][Br]) was obtained. Iron acetate (5 mmol) was then added into this ionic liquid with stirring at room temperature for 24 h to give ionic liquid/iron (Fe/IL) complex.

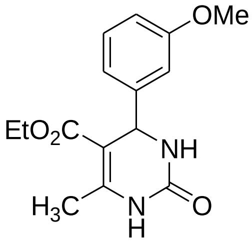
2.2. *Preparation of the PEt@Fe/IL composite*

The immobilization of Fe/IL complex on polyethylene was achieved via coacervation approach [32]. Firstly, the high-density polyethylene (HDPE) was dissolved in xylene at reflux conditions in a container equipped with a condenser, mechanical stirrer and thermometer. Then, the pre-prepared ionic liquid/Fe (Fe/IL) complex was added to the HDPE solution and mixing process was continued for 2 hours. Then the resulting mixture was precipitated into methanol at 4 °C. The obtained precipitate was finally washed with methanol several times and dried for 24 h at 90 °C to give PEt@Fe/IL composite.

2.3. *General procedure for the Biginelli reaction using PEt@Fe/IL catalyst*

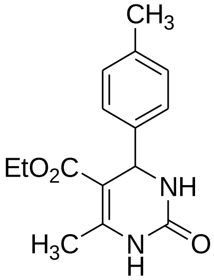
For this, the PEt@Fe/IL catalyst (0.75 mol %) was added to a homogeneous mixture of aldehyde (2 mmol), ethylacetoacetate (2 mmol) and urea (3 mmol). This was then magnetically stirred at 80 °C while the reaction progress was monitored by thin layer chromatography (TLC). After completion of the process, hot ethanol (10 mL) was added to the reaction flask and the obtained solution was hotly filtered. The filtrate was then placed in an ice bath to precipitate crude crystals. These were recrystallized in ethanol to give pure Biginelli products in high to excellent yields. The products were characterized by IR, ^{1}H-NMR, ^{13}C-NMR and *via* comparison of their melting points with the reported ones. Spectroscopic data of new compounds are as following:

5- Ethoxycarbonyl-6-methyl-4-(3-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one:



Mp: 217-220 °C; IR (KBr, cm^{-1}): 3245, 3118, 2933, 1726, 1704, 1577, 1646, 1222, 1086. ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 ^{o}C, TMS) δ (ppm): 1.10 (t, 3H, OCH$_2$C**H$_3$**, j=7.2 Hz), 2.26 (s, 3H, CH$_3$), 3.74 (s, 3H, OCH$_3$), 3.97 (q, 2H ,OC**H$_2$**CH$_3$, j=7.2 Hz), 5.11 (s, 1H, CH), 6.88-7.17 (m, 4H, Ar–H), 7.69 (s, 1H, NH), 9.17 (s, 1H, NH); ^{13}C NMR (100.63 MHz, DMSO-d$_6$) δ (ppm): 165.9, 158.9, 152.7, 152.6, 148.5, 148.4, 137.5, 127.9, 114.2, 100.1, 59.6, 55.5, 53.8, 18.2, 14.6.

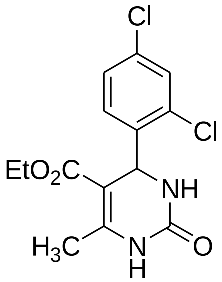
5-Ethoxycarbonyl-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin- 2(1H)-one:



Mp: 213-214 ˚C; IR (KBr, cm^{-1}): 3247, 3112, 2927, 1724, 1707, 1459, 1649, 1220. ^{1}H-NMR (400 MHz, DMSO-d$_6$, 25 ^{o}C, TMS) δ (ppm): 1.10 (t, 3H, OCH$_2$C**H$_3$**, j=6.8 Hz), 2.25 (s, 3H, CH$_3$), 2.28 (s, 3H, CH$_3$), 3.97 (q, 2H ,OC**H$_2$**CH$_3$, j=6.8 Hz), 5.11 (s, 1H, CH), 7.1 (s, 4H, Ar-H), 7.7 (s, 1H, NH), 9.17 (s, 1H, NH);

^{13}C NMR (100.63 MHz, DMSO) δ (ppm): 165.8, 152.7, 148.6, 142.4, 136.9, 129.4, 126.6, 99.9, 59.6, 54.12, 21.1, 18.2, 14.6.

5- Ethoxycarbonyl -6-methyl-4-(2,4-dichlorophenyl)-3,4-dihydropyrimidin-2(1H)-one :



Mp: 246-248 ˚C; IR (KBr, cm^{-1}): 3243, 3112, 2956, 2931, 1725, 1706, 1648, 1614, 1511, 1222, 1087.

^{1}H-NMR (400 MHz, DMSO-d$_6$, 25 ºC, TMS) δ (ppm): 1.10 (t, 3H, OCH$_2$C**H$_3$**, j=7 Hz), 2.27 (s, 3H, CH$_3$), 4.00 (q, 2H ,OC**H$_2$**CH$_3$, j=7 Hz), 5.16 (s, 1H, CH), 7.24-7.35 (m, 3H, Ar–H), 7.76 (s, 1H, NH), 9.22 (s, 1H, NH).

^{13}C-NMR (100.63 MHz, DMSO) δ (ppm): 165.83, 160.5, 152.7, 148.8, 145.3, 136.9, 128.9, 127.8, 126.7, 99.8, 59.7, 54.4, 18.5, 14.5.

2.4. *General procedure for the recovery of the PEt@Fe/IL catalyst in the Biginelli reaction*

For this, 0.75 mol% of PEt@Fe/IL catalyst was added to a flask containing benzaldehyde, ethylacetoacetate and urea. The obtained mixture was then magnetically stirred at 80 °C. The reaction progress was monitored by TLC. After completion of the reaction, hot ethanol was added and the obtained solution was hotly filtered. The recovered catalyst was completely washed with ethanol. Then this catalyst was reused at the same conditions as the first run for at least 7 times and delivered corresponding Biginelli product in high to excellent yield.

3. Results and discussion

The PEt@Fe/IL was prepared by immobilization of iron/ionic liquid complex onto polyethylene via coacervation method (Scheme 1) [32]. The structural and chemical properties of the material was investigated with several techniques such as DRIFTs, SEM, TGA and EDX. Firstly, the DRIFT spectroscopy was used to determine the functional groups of the material (Figure 1). The absorption peaks of organic functional groups were observed at 2915 and 2850 cm^{-1} (aliphatic C-H stretching vibrations), 1629 cm^{-1} (C=N stretching vibration of imidazolium ring), 1525 cm^{-1} (C=C stretching vibration of imidazolium ring) 1473 cm^{-1} (CH_2 bending vibration), 1461 cm^{-1} (C-H deformation vibrations), 1367 cm^{-1} (CH_3 bending vibration), and 720 cm^{-1} (CH_2 rocking), respectively. These observations successfully confirm well immobilization of alkyl imidazolium ionic liquid groups onto polyethylene. Thermal gravimetric analysis (TGA) of the PEt@Fe/IL was next carried out from room temperature to 800 °C (Figure 2). This analysis demonstrated a weight loss of 1.37% below 250 °C which is attributed to the removal of water and methanol. The second weight loss between 300 and 400 °C corresponding to elimination of ionic liquid groups which are located onto/into polymer material. The main weight loss of 92.55 in the range of 400–500 °C corresponding to the decomposition and removal of polyethylene organic moieties. These data also confirm the successful immobilization of the ionic liquid functional groups in the material network and also verify high thermal stability of the catalyst.

The PEt@Fe/IL was also analyzed by inductively coupled plasma/optical emission spectroscopy (ICP-OES). According to this analysis, the amount of iron in the catalyst was 0.5 percent (0.09 mmol Fe/g) confirming that the iron species have been well immobilized on the material. The results of energy-dispersive X-ray (EDX) spectroscopy elemental microanalysis of the PEt@Fe/IL also confirmed the presence of C, N, and Fe in the catalyst (Figure 3). This is in good agreement with DRIFT and TGA analyses confirming successful immobilization of IL/Fe complex on polymer support. In the next study, X-ray photoelectron spectroscopy (XPS) of the PEt@Fe/IL material was performed to identify true catalyst in the reaction process. The XPS signals versus binding energy clearly showed Fe-peaks at 711.02 eV (for Fe $2p_{3/2}$) and 717.01 eV (for Fe $2p_{1/2}$) proving the successful immobilization of Fe-complex in the material network (Figure 4). This result is reasonably far from metallic iron (with Fe $2p_{3/2}$ of 706.75) and is very close to those of FeX_3 with Fe $2p_{3/2}$ of 711 eV [33]. This means that the understudied iron is strongly bound to electronegative atoms and its oxidation state is as Fe (III). Based these observations, we conclude that the actual catalyst is ([MOIM][Fe(OAc)$_3$Br]).

The scanning electron microscopy (SEM) analysis was next carried out to study morphology of the material. The SEM image of the PEt@Fe/IL before reaction (Figure 5a) revealed the presence of regular particles with uniform morphology. The SEM image of the PEt@Fe/IL material after reaction showed the particles with morphology different with those of its parent (Figure 5b) confirming a change in material particles during reaction process.

In the next stage, the activity of characterized PEt@Fe/IL was tested in the three component Biginelli condensation of benzaldehyde, urea and ethylacetoacetate according to Table 1. To find optimal reaction conditions, firstly the effect of solvent, temperature and catalyst loading was studied.

As presented in Table 1, trace product was obtained in the absence of the catalyst after 90 min (entry 1) indicating that the catalyst is necessary for the reaction. This study showed that with increasing amount of the catalyst from 0.2 to 0.75 mol%, the yield of the desired product is remarkably increased indicating significant effect of the catalyst loading in the reaction progress (Table 1, entries 2–4).

The reaction was also affected by temperature and the best result was obtained at 80 °C (Table 1, entries 4–6). Our study was also extended to observe the effect of solvent on the reaction (Table 1, entries 7-10). As shown, the polar solvent such as ethanol, acetonitrile and tetrahydrofuran resulted in 71%, 68% and 57% yield, respectively, while 15% yield of the product was obtained by using toluene. This may be attributed to the better solubility of the starting materials in the polar solvents. Interestingly, under solvent-free media at similar conditions and time as above, the reaction was completed and a quantitative yield of corresponding Biginelli product was obtained (Table 1, entry 4).

According to the aforementioned results, the use of 0.75 mol% of PEt@Fe/IL catalyst at 80 °C under solvent-free media were selected as optimum conditions (Table 2). As shown, various aromatic aldehydes have been successfully employed in this reaction which is a good evidence to the large scope of this catalyst system. This condensation process was fairly robust and several functionalities such as nitro, chloro, bromo, hydroxyl, methyl and methoxy survived during the course of reaction in a single step. It is also clear that, aromatic aldehydes containing either electron-withdrawing or electron-donating substituents afford high yields of products with high purity. As presented in Table 2, electronic effects were observed: benzaldehydes containing electron-donating group required lower reaction times to deliver the corresponding products in high yield, while those with an electron-withdrawing group gave high yield in longer reaction times. Interestingly, *ortho*-substituted benzaldehydes which due to steric effects are usually less-reactive in organic reactions, also afforded the corresponding 3,4-dihydropyrimidin-2(1H)-ones in relatively high yields, whether they had an electron-donating or an electron-withdrawing group (Table 2, entries 4, 5, 7, 11, 14). These observations confirm high efficiency of the catalyst for the conversion of a broad range of aromatic aldehydes to their corresponding Biginelli products applicable in different area of chemistry and biochemistry. Where an aliphatic aldehyde, such as isoporopyl aldehyde, was used as substrate, only a trace conversion was observed.

In the next study, the recycling performance of the PEt@Fe/IL catalyst was tested in the condensation of benzaldehyde, urea and ethylacetoacetate under optimized conditions. For this, after the reaction was completed, the mixture was filtered and thoroughly washed with hot ethanol. The recovered catalyst was then reused in the next run under the same conditions as the first run. The more experiments were performed as before and the results illustrated that the catalyst could be recovered and reused for at least 7 times without significant decrease in activity (Table 3). This observation successfully confirms high recycling efficiency of the PEt@Fe/IL catalyst which is a noteworthy property in economic and environmental points of view.

Although according the later test, no significant reduce in the catalyst performance was observed, however, to verify the leaching of active iron species from the material during reaction process, in the next study a hot filtration test was performed in the reaction of benzaldehyde, urea and ethylacetoacetate after about 45% of the coupling reaction was completed. The catalyst free filtrate was then transferred to another flask and the reaction progress was monitored under the same conditions as before. Interestingly, after 2 h only 5% additional conversion was observed in the coupling reaction. Moreover, the atomic absorption spectroscopy showed no presence of iron species in the filtrate. These significantly confirm well immobilization and high stability of the catalytic species onto polymer support as well as prove that the catalyst operates in a heterogeneous manner.

In the final study, to explore the advantages of PEt@Fe/IL catalyzed synthesis of 3,4-dihydropyrimidin-2(1H)-one, the results obtained under our optimized conditions were compared with those reported in the literature using other catalysts (Table 4). As shown, the most of the former catalytic systems have been performed in the organic solvents at higher reaction times than the PEt@Fe/IL catalyst. Moreover, in the most cases of the previous works, the recycling times of the catalyst are lower than present ones. These significantly confirm high efficiency and recoverability of the designed catalytic system in comparison with former systems.

4. Conclusion

In summary, we described here an efficient method for the synthesis of 3,4-dihydropyrimidinones in a PEt@Fe/IL catalyzed reaction of aldehydes, alkylacetoacetates and urea under solvent free conditions. The material characterization showed high thermal stability of the catalyst and also well immobilization of ionic liquid/Fe complex onto PEt polymer support. The catalyst demonstrated excellent reactivity for the Biginelli condensation of a variety of different electron-withdrawing and electron-donating aromatic aldehydes and delivered corresponding 3,4-dihydropyrimidinone products in high to excellent yields. The simplicity of the reaction, easy separation of catalyst and products from the reaction mixture, high yields and short response time make this an improved protocol than existing methods. In addition, the catalyst could be easily recovered and reused several times without significant loss in efficiency. Therefore, the use of PEt@Fe/IL as catalyst not only makes the reaction economical viable but also help to reduce environmental pollution to achieve environmentally friendly processes.

Acknowledgements

The authors acknowledge the Yasouj University, Iran National Science Foundation (INSF) and the Graduate School and Research Council of the Payame Noor University for supporting this work.

References

[1] P. Biginelli, Chem. Ber. 24 (1891) 1317-1319.

[2] F. Makaev, E. Styngach, V. Muntyanu, S. Pogrebnoi, Russ. J. Org. Chem. 43 (2007) 1512-1515.

[3] (a) G.C. Rovnyak, S.D. Kimball, B. Bever, J. Med. Chem. 38 (1995) 119-129. (b) K.S. Atwal, C.G. Rovnyak, S.D. Kimball, J. Med. Chem. 33 (1990) 2629-2635. (c) H. Cho, M. Ueda, K. Shima, J. Med. Chem. 32 (1989) 2399-2406.

[4] (a) G.C. Rovnyak, K.S. Atwal, S.D. Kimball, J. Med. Chem. 35 (1992) 3254-3263. (b) K.S. Atwal, B.N. Swanson, S.E. Unger, J. Med. Chem. 34 (1991) 806-811.

[5] D.R. Sidler, R.D. Larsen, M. Chartrain, N. Ikemoto, C.M. Roberge, C.S. Taylor, W. Li, G.F. Bills, PCT Int. Appl. WO 99 07695, 1999.

[6] S.V. Ryabukhin, A.S. Plaskon, E.N. Ostapchuk, D.M. Volochnyuk, Synthesis 3 (2007) 417-427.

[7] I. Cepanec, M. Litvic, A. Bartolincic, Tetrahedron 61 (2005) 4275-4280.

[8] J.H. Schauble, E.A. Trauffer, P.P. Deshpande, R.D. Evans, Synthesis 8 (2005) 1333-1339.

[9] H. Hazarkhani, B. Karimi, Synthesis 8 (2004) 1239-1242.

[10] J. Lu, Y.J. Bai, Synthesis 4 (2002) 466-470.

[11] (a) C. O. Kappe, Acc. Chem. Res. 33, (2000) 879-888.(b) J. Azizian, A. A. Mohammadi, A. R. Karimi, M. R. Mohammadizadeh, App. Catal. A: Gen. 300, (2006), 85–88. (c) S. L. Jain, J. K. Joseph, S. Singhal, B. Sain, J. Mol. Catal. A: Chem. 268, (2007), 134–138. (d) S. L. Jain, V. V. D. N. Prasad, B. Sain, Catal. Commun. 9, (2008), 499 –503. (e) P. Li, S. Regati, R. J. Butcher, H. D. Arman, Z. Chen, S. Xiang, B. Chen, C.-G. Zhao, Tetrahedron Lett. 52 *(*2011), 6220-6222. (f) R. K. Sharma, D. Rawat, Inorg. Chem. Commun. 17, (2012), 58–63. (g) M. J. Climent, A. Corma, S. Iborra, RSC Adv, 2 (2012) 16-58. (h) J. Mondal, T. Sen, A. Bhaumik, Dalton Trans. 41 (2012) 6173-6181. (i) R. Tayebee, M. M. Amini, M. Ghadamgahi, M. Armaghan, J. Mol. Catal. A: Chem. 366, (2013), 266–274. (j) F. Zamani, S. M. Hosseini, S. Kianpour, Solid State Sci. 26, (2013), 139–143. (k) M. Pramanik, A. Bhaumik, ACS Appl. Mater. Interfaces 6 (2014), 933-941. (l) A. Dhakshinamoorthy, H. Garcia, Chem. Soc. Rev. 43, (2014), 5750–5765.

[12] (a) N. E. Leadbeater, M. Marco, Chem. Rev., 102, (2002), 3217–3274. (b) M. Lei, D-D. Wu, H-G. Wei, Y-G. Wang, Synth. Commun. 39 (2009) 475-483. (c) R. J. Kalbasi, A. R. Massah, B. Daneshvarnejad, App. Clay Sci. 55, (2012) 1-9.

[13] (a) D. Elhamifar, A. Shábani, Chem. Eur. J. 20 (2014) 3212-3217. (b) D. Elhamifar, E. Nazari, ChemPlusChem 80 (2015) 820-826. (c) D. Elhamifar, F. Hosseinpoor, B. Karimi, S. Hajati, Microporous Mesoporous Mater. 204 (2015) 269-275.

[14] D. Elhamifar, M. Nasr-Esfahani, B. Karimi, R. Moshkelgosha, A. Shábani, ChemCatChem 6, (2014), 2593–2599.

[15] H. Zois, L. Apekis, Y.P. Mamunya, Macromol. Symp. 194 (2003) 351-359.

[16] Y.P. Mamunya, H. Zois, L. Apekis, E.V. Lebedev, Powder Technol. 140 (2004) 49-55.

[17] K. Zhu, S. Schmauder, Comput. Mater. Sci. 28 (2003)743-748.

[18] M. Rusu, N. Sofian, D. Rusu, Polym. Test. 20 (2001) 409-417.

[19] P. Cheang, K.A. Khor, Mater. Sci. Eng. A345 (2003) 47-54.

[20] T. Ahmad, O. Mamat, W. J. N. S. E. 1 (2011) 7-14.

[21] K.M. Driller, H. Klein, R. Jackstell, M. Beller, Angew. Chem. Int. Ed. 48 (2009) 6041-6044.

[22] G. Paolucci, M. Bortoluzzi, M. Napoli, P. Longo, J. Mol. Catal. A: Chem. 287 (2008) 121-127.

[23] S. Tangestaninejad, M.H. Habibi, V. Mirkhani, M. Moghadam, G. Grivani, Inorg. Chem. Commun. 9 (2006) 575-578.

[24] X. Shi, Q. Hu, F. Wang, W. Zhang, P. Duan, J. Catal. 337(2016) 233-239.

[25] M. Li, Y. Lei, N. Sheng, T. Ohtsuka, J. Power Sources 294 (2015) 420-429.

[26] M. Moghadam, S. Tangestaninejad, M.H. Habibi, V. Mirkhani, J. Mol. Catal. A: Chem.(2004) 9-12.

[27] R. Ferro, S. Milione, T. Caruso, A. Grassi, J. Mol. Catal. A Chem. 307 (2009) 128-133.

[28] R. Luo, A. Sen, Macromolecules 41 (2008) 4514-4518.

[29] K. Hooshyari, M. Javanbakht, M. Adibi, Electrochim. Acta 205(2016) 142-152.

[30] A.H. Jadhav, G.M. Thorat, K. Lee, A.C. Lim, H. Kang, J.G. Seo, Catal. Today 265 (2016) 56-67.

[31] S. Gou, T. Yin, L. Yan, Q. Guo, Colloids Surf. A 471 (2015) 45-53.

[32] D. B. Siano, J. Bock, J. J. Colloid Interface Sci. 90, (1982)359-372. (b) N. Pawar, H. B. Bohidar, Adv. Colloid Interface Sci. 167, (2011) 12-23. (c) D. Priftis, K. Megley, N. Laugel, M. Tirrell, J. Colloid Interface Sci. 398, (2013) 39–50. (d) X. Yang, N. Gao, L. Hu, J. Li, Y. Sun, J. Food Eng. 161, (2015), 87-93. (e) N. S. Girardi, D. García, S. N. Robledo, M. A. Passone, A. Nesci, M.Etcheverry, Ind. Crops Prod. 92, (2016) 93-101. (f) C. E. Sing, Adv. Colloid Interface Sci. (2016), http://dx.doi.org/10.1016/j.cis.2016.04.004.

[33] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenberg, Handbook of X-ray Photoelectron Spectroscopy, PerkinElmer, Eden Prairie, Minn, USA, 1979.

[34] Y. Ma, C. Qian, L. Wang, M. Yang, J. Org. Chem. 65 (2000) 3864-3868.

[35] J. Lu, H. Ma, Synlett 1 (2000) 63-64.

[36] N.Y. Fu, Y.F. Yuan, Z. Cao, S.W. Wang, J.T. Wang, C. Peppe, Tetrahedron Lett. 58 (2002) 4801-4807.

[37] M. Nasr-Esfahani, M. Taei, RSC Adv. 5 (2015) 44978-44989.

[38] C.J. Liu, J.D. Wang, Molecules 14 (2009) 763–770.

[39] F.L. Zumpe, M.B. Flu, K. Schmitz, A. Lender, Tetrahedron Lett. 48 (2007) 1421-1423.

[40] Z.T. Wang, S.C. Wang, L.W. Xu, Helv. Chim. Acta 88 (2005) 986-989.

[41] X. Wang, Z. Quan, F. Wang, M. Wang, Z. Zhang, Z. Li, Synth. Commun. 36 (2006) 451-456.

[42] A. Pourjavadi, S.H. Hosseini, R. Soleyman, J. Mol. Catal. A: Chem. 365 (2012) 55-59.

[43] Z.J. Quan, Y.X. Da, Z. Zhang, X.C. Wang, Catal. Commun. 10 (2009) 1146-1148.

[44] S. Verma, S.L. Jain, B. Sain, Tetrahedron Lett. 51 (2010) 6897-6900.

[45] S. Palaniappan, A. John, J. Mol. Catal. A: Chem. 233 (2005) 9-15.

Figures caption:

Fig. 1. DRIFT spectrum of PEt@Fe/IL.

Fig. 2. Thermal gravimetric analysis (TGA) of the PEt@Fe/IL

Fig. 3. Energy dispersive X-ray (EDX) spectroscopy of the PEt@Fe/IL

Fig. 4. XPS analysis of PEt@FE/IL catalyst

Fig. 5. Scanning electron microscopy (SEM) image of the PEt@Fe/IL (a) before and (b) after the reaction

Scheme 1. Preparation of the PEt@Fe/IL composite

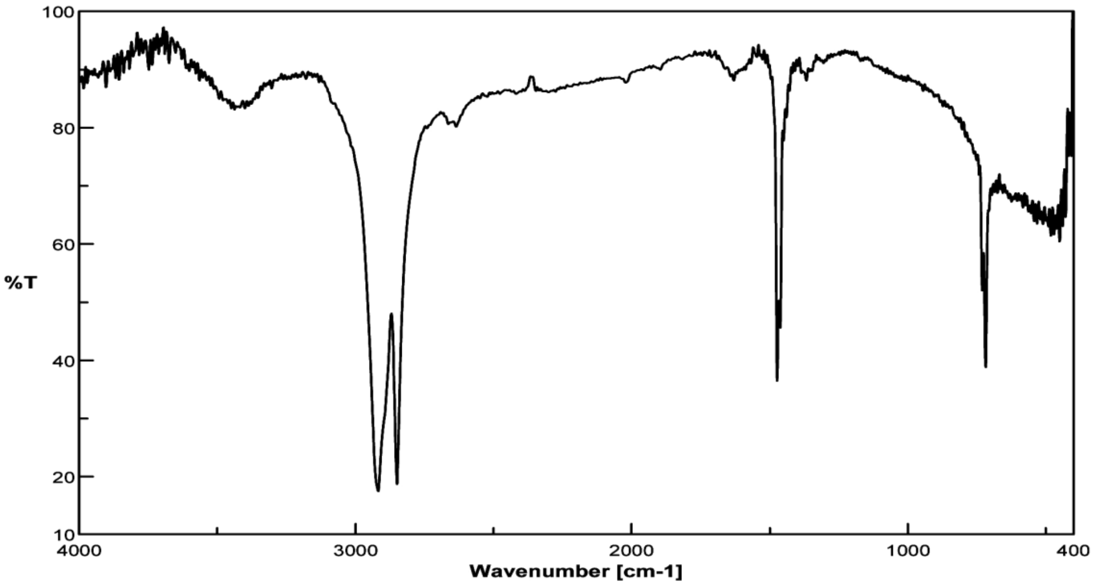


Fig. 1.

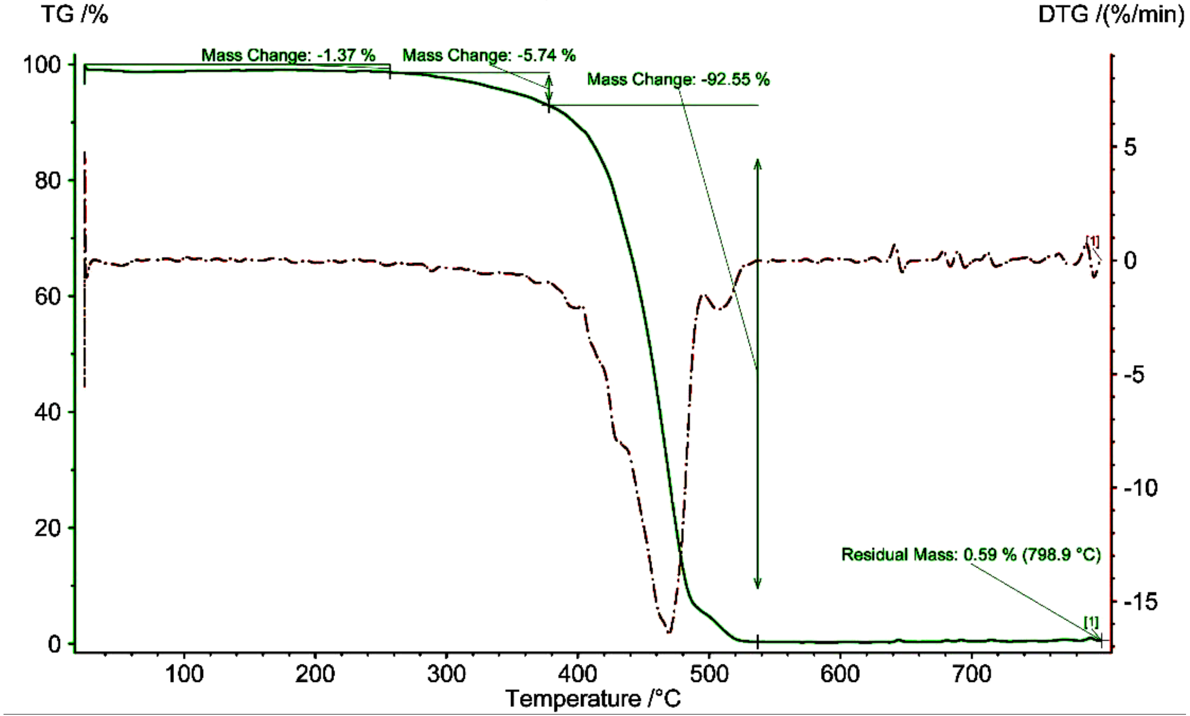

TG /%
DTG /(%/min)
Mass Change: -1.37 %
Mass Change: -5.74 %
Mass Change: -92.55 %
Residual Mass: 0.59 % (798.9 °C)
[1]
[1]
100
80
60
40
20
0
5
0
-5
-10
-15
100
200
300
400
500
600
700
Temperature /°C

Fig. 2.

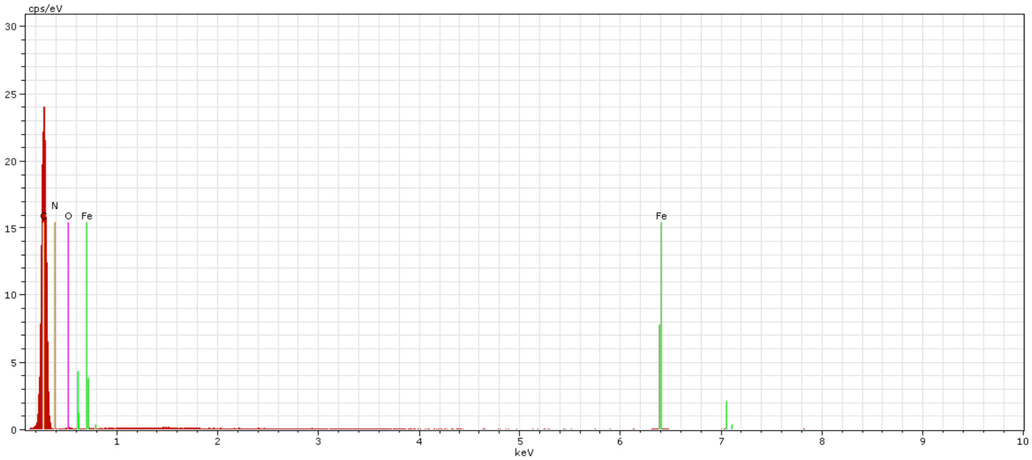

cps/eV
30
25
20
15
10
5
0
C
N
O
Fe
Fe
1
2
3
4
5
6
7
8
9
10
keV

Fig. 3.

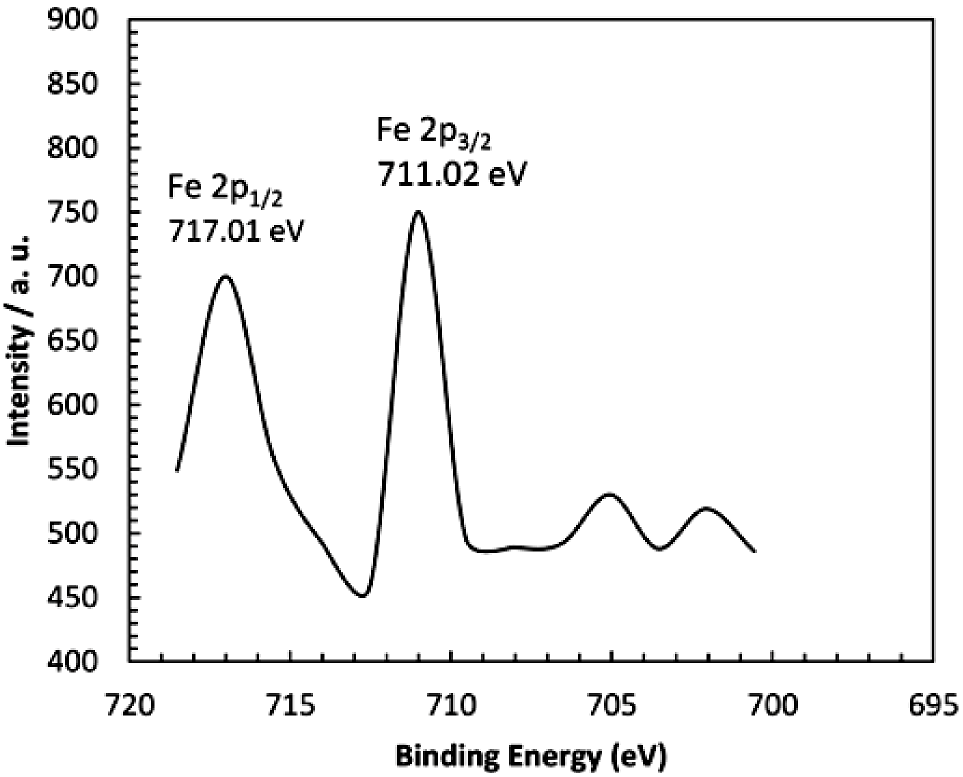

Intensity / a. u.
900
850
800
750
700
650
600
550
500
450
400
720
715
710
705
700
695
Binding Energy (eV)
Fe 2p$_{1/2}$
717.01 eV
Fe 2p$_{3/2}$
711.02 eV

Fig. 4

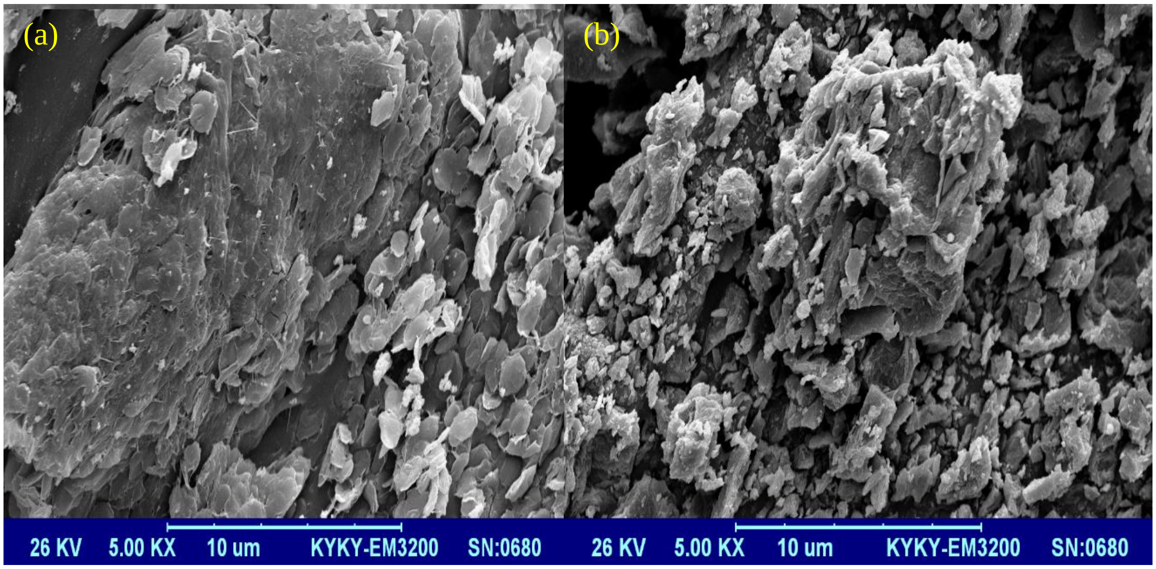
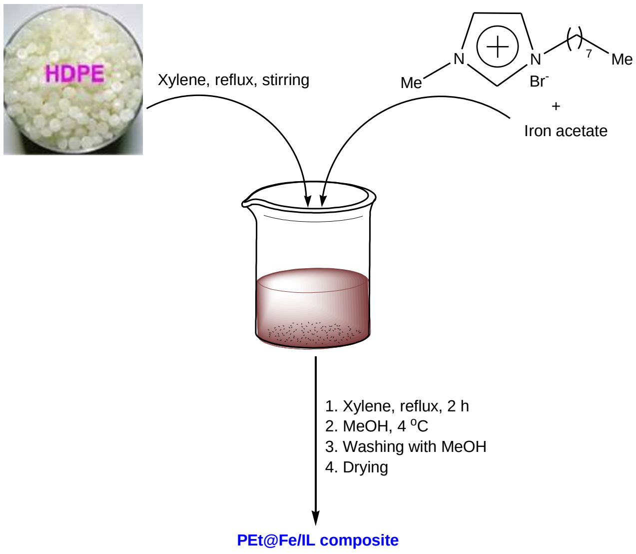

(a)
(b)
26 KV 5.00 KX 10 um KYKY-EM3200 SN:0680
26 KV 5.00 KX 10 um KYKY-EM3200 SN:0680

Fig. 5.


HDPE
Xylene, reflux, stirring
Me
N
N
7
Me
Br⁻
+
Iron acetate
1. Xylene, reflux, 2 h
2. MeOH, 4 °C
3. Washing with MeOH
4. Drying
PEt@Fe/IL composite

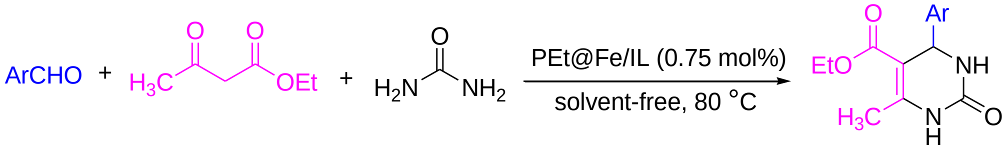
Scheme 1

Table 1. The effect of catalyst loading, temperature and solvent in the Biginelli reaction of benzaldehyde with urea and ethylacetoacetate[a]

Entry	Catalyst	Catalyst loading (mol %)	T (°C)	Solvent	Yield (%)[b]
1	No catalyst	-	80	-	Trace
2	PEt@Fe/IL	0.2	80	-	27
3	PEt@Fe/IL	0.5	80	-	55
4	**PEt@Fe/IL**	**0.75**	**80**	-	**95**
5	PEt@Fe/IL	0.75	30	-	10
6	PEt@Fe/IL	0.75	50	-	45
7	PEt@Fe/IL	0.75	Reflux	EtOH	71
8	PEt@Fe/IL	0.75	Reflux	CH_3CN	68
9	PEt@Fe/IL	0.75	80	Toluene	15
10	PEt@Fe/IL	0.75	Reflux	THF	57

[a] Reaction conditions: benzaldehyde (1 mmol), ethylacetoacetate (1 mmol), urea (1.5 mmol), 90 min. [b] Isolated yield.

Table 2. Preparation of dihydropyrimidinone derivatives in the presence of PEt@Fe/IL catalyst [a]



Entry	Ar	Time (min)	Yield (%)[b] [TON][c]	Found M. p. (°C)	Reported M. p. (°C)
1	C_6H_5	90	95 [126.7]	200-202	201-203 [34]
2	4-Cl–C_6H_4	110	94 [125.3]	209-210	210-212 [34]
3	3-Cl–C_6H_4	110	90 [120]	190-193	192-193 [35]
4	2-Cl–C_6H_4	120	83 [110.7]	218-221	222-224 [36]
5	2,4-Cl–C_6H_4	120	85 [113.3]	246-248	248-250 [37]
6	3-Br-C_6H_4	110	89 [118.7]	188-190	190-192 [38]
7	2-Br–C_6H_4	110	84 [112]	205-207	206-208 [34]
8	4-NO_2–C_6H_4	100	95 [126.7]	207-208	207-210 [34]
9	3-NO_2–C_6H_4	100	89 [118.7]	228-231	229-231 [36]
10	4-CH_3–C_6H_4	120	92 [122.7]	213-214	215-216 [36]
11	2-CH_3–C_6H_4	120	92 [122.7]	207-209	208-210 [36]
12	4-MeO–C_6H_4	120	91 [121.3]	198-200	199-201 [34]
13	3-MeO–C_6H_4	120	93 [124]	218-219	220-221 [39]
14	2-MeO –C_6H_4	120	85 [113.3]	257-260	257-258 [39]

[a] Reaction conditions: aldehyde (1 mmol), ethylacetoacetate (1 mmol), urea (1.5 mmol). [b] Isolated yield.[c] TON=turnover number (defined as mmol of product/mmol of catalyst).

Table 3. Reusability of the PEt@Fe/IL catalyst in the Biginelli reaction of benzaldehyde with ethylacetoacetate and urea

Run	Time (min)	Conversion	Run	Time (min)	Conversion
1	90	97	5	110	92
2	95	96	6	115	90
3	105	96	7	115	85
4	110	94	8	120	83

Table 4. Comparison of catalytic activity of PEt@Fe/IL with other catalysts reported in the literature for the synthesis of 3,4-dihydropyrimidinones

Entry	Catalyst	Conditions	Time (h)	Recovery times	Ref.
1	$PsMimPF_6$	AcOH, 100 °C	2	-	[40]
2	$PEG\text{-}SO_3H$	Microwave oven, 100 °C	0.1	-	[41]
3	Poly(SIL)	EtOH, 80 °C	7	5	[42]
4	$PS\text{-}PEG\text{-}SO_3H$	Dioxane/2-propanol, reflux	10	-	[43]
5	PEG.TUD II	Solvent-free, 50 °C	10-15	-	[44]
6	$PANI–HBF_4–DHS$	EtOH, reflux	6	2	[45]
7	PEt@Fe/IL	Solvent-free, 80 °C	1.5	7	This work

Abbreviations: $PsMimPF_6$: polystyrene–methylimidazolium hexafluorophosphate, PEG: poly(ethyleneglycol), Poly(SIL): poly(l-vinyl-3-(3-sulfopropyl) imidazolium hydrogen sulfate), PS-PEG: polystyrene–poly(ethylene glycol) PEG.TUD II: polyethylene glycol and thiourea dioxide, $PANI–HBF_4–DHS$: polyaniline–fluoroboric acid–dodecylhydrogensulfate