Alkyl-imidazolium Based Organosilica Supported Fe/Porphyrin Complex: As Novel, Highly Efficient and Reusable Catalyst for the Unsymmetrical Hantzsch Reaction

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Abstract: A noble alkyl-imidazolium ionic liquid based organosilica supported Fe/*meso*-tetrakis(4-sulfonatophenyl)porphyrin complex (ILOS@Fe/TSPP) is prepared, characterized and its catalytic efficiency is studied in the unsymmetrical Hantzsch reaction. The ILOS@Fe/TSPP was prepared by hydrolysis and co-condensation of 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride under acidic conditions followed by treatment with Fe/*meso*-tetrakis(4-sulfonatophenyl)porphyrin complex at ambient temperature. The material was characterized with TGA, EDX, SEM, TEM, XRD and DRIFT analyses. The ILOS@Fe/TSPP was successfully applied as powerful catalyst in the Hantzsch reaction for the preparation of a set of different derivatives of polyhydroquinolines in high to excellent yields. This catalyst was recovered and reused several times without important decrease in its activity. Furthermore, compared to the classical studies, this study consistently demonstrated the advantages of low catalyst loading, free-solvent media, short reaction times and simple purification of products.

Keywords: Ionic liquid based organosilica, supported Fe/porphyrin catalyst, Hantzsch reaction, recoverable and reusable catalyst

1. Introduction

Hantzsch synthesis of polyhydroquinolines is one of the most significant multi-component process due to its key role in the production of pharmacologically useful compounds [1-10]. Some pharmacological activities of the Hantzsch products include calcium channel blockers, vasodilator, bronchodilator, antiatherosclerotic, antitumor, geroprotective, hepatoprotective, and antidiabetic agents [3-10]. This method generally involves one-pot condensation of aldehydes with β -dicarbonyls, activated methylenes and amine sources under acidic conditions [1, 2]. In view of the importance of polyhydroquinolines, numerous methods for their synthesis have been reported using conventional heating and refluxing approaches in the presence of acid catalysts under homogeneous conditions [11-16]. Some of these developing catalysts include TMSCl [11], TMSI [11], hafnium (IV) bis(perfluorooctanesulfonyl)imide complex $[\text{Hf}(\text{NPf}_2)_4]$ [12], $\text{Yb}(\text{OTf})_3$ [13], cerium (IV) ammonium nitrate [14], Bu_4NHSO_4 [15], ionic liquids [16], iodine [17], PTSA-SDS [18] and boronic acids [19, 20]. However, these methods suffer from drawbacks such as a long reaction time, the use of large amount of volatile organic solvents, catalyst recovery, product separation and harsh refluxing conditions. To overcome these restrictions, more recently several supported acid catalysts such as ordered mesoporous silicas [21], silica-supported acids [22], polymers [23], ZnO nanoparticles [24], Ni-nanoparticles [25], HY-zeolite [26] and montmorillonite K10 clay [27] have been applied in this regard. However, these also suffer from disadvantages such as high catalyst loading and the use of volatile organic solvents. Therefore, it

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4 is still necessary to develop an efficient and versatile catalyst for the preparation of
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6 polyhydroquinolines under better conditions than before.
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11 On the other hand, ionic liquids (ILs) are one of the most significant class of organic salts that
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13 have attracted considerable attentions due to their unique properties such as high thermal
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15 stability, tunable physiochemical properties, broad liquid range and their excellent ability for
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17 dissolving a wide range of organic and inorganic compounds [28-30]. Accordingly, ionic liquids
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19 have potential applications especially as solvent and catalyst in different organic processes [28-
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21 30]. However, these compounds are usually **expensive and** due to high viscosity of them, the
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23 bulk ionic liquid may suffer from slow diffusion, causing the main part of the reaction to proceed
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25 in a small fraction of ILs called the “diffusion layer” [31, 32a]. Therefore, recently several
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27 attempts have been done to remove these restrictions in a typical chemical process. One of
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29 successful approaches in this regard is supporting of ionic liquids onto/into reusable and
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31 recoverable supports such as silica, alumina and polymers. This immobilization has been
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33 achieved *via* different methods such as simple impregnation, chemical attachment, co-
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35 condensation and encapsulation or pore trapping. Along this line, we have developed a novel
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37 strategy for the successful immobilization of alkyl imidazolium based ionic liquids in the silica
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39 framework. These materials were applied as powerful and reusable support for the catalytic and
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41 adsorption processes [31, 32]. In continuation of these studies, more recently we also reported a
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43 novel manganese-containing ionic liquid based periodic mesoporous organosilica (Mn@PMO-
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45 IL) nanocatalyst for the preparation of a wide range of polyhydroquinoline derivatives under
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47 solvent-free media [33]. This catalyst was recovered and reused several times without significant
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49 decrease in its efficiency. As part of these studies and according to importance of
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polyhydroquinolines in biological and pharmacological processes, herein, for the first time a novel ionic liquid based organosilica supported Fe/TSPP complex is prepared, characterized and its catalytic performance is developed in the preparation of polyhydroquinolines under solvent free media and very short times (Scheme 1).

2. Experimental Section

2.1. Preparation of ionic liquid based organosilica supported Fe/TSPP (ILOS@Fe/TSPP) catalyst

Ionic liquid based organosilica (ILOS) was prepared by simultaneous hydrolysis and condensation of 1,3-bis(trimethoxysilylpropyl) imidazolium chloride under acidic conditions [31]. Iron/*meso*-tetrakis(4-sulfonatophenyl)porphyrin (Fe/TSPP) complex was also synthesized by sulfonation of tetraphenyl porphyrin (TPP) with concentrated H₂SO₄ followed by treatment with Fe(OAc)₂·2H₂O [34]. Ionic liquid based organosilica supported Fe/TSPP complex (ILOS@Fe/TSPP) was prepared by treatment of Fe/TSPP with ILOS in distilled water as follows: Firstly, Fe/TSPP (2 mmol) was dissolved in distilled water to give a uniform amethystine solution (Figure 1a). ILOS (1 g) was also homogeneously dispersed in water (Figure 1b). Then, the Fe/TSPP solution was added to the ILOS vessel and the obtained mixture was stirred at room temperature for 24 h. In this step, a light brown mixture was observed (Figure 1c). After that, the resulting mixture was filtered and repeatedly washed with water to remove unsupported Fe/TSPP complex. Finally, the obtained material was dried at 70 °C to give a light brown powder called ILOS@Fe/TSPP (Figure 1d).

2.2. General procedure for the preparation of polyhydroquinolines in the presence of ILOS@Fe/TSPP catalyst

For the preparation of polyhydroquinolines, aldehyde (1 mmol), dimedone (1 mmol), ammonium acetate (1.2 mmol), alkylacetoacetate (1 mmol) and ILOS@Fe/TSPP catalyst (0.6 mol%) were mixed and stirred thoroughly in a round-bottomed flask. After a uniform mixture was obtained, it was heated at 75 °C with concomitant stirring. After completion of the reaction, monitored by TLC, warm ethanol (10 mL) was added and the obtained mixture was filtered and repeatedly washed with ethanol. The solvent was then evaporated and the crude products were recrystallized in ethanol to give pure crystals in high to excellent yield. The products were characterized by IR, ¹H-NMR, ¹³C-NMR and *via* comparison of their melting points with the reported ones.

2.3. General procedure for the recovery of ILOS@Fe/TSPP catalyst

To do this, benzaldehyde (1 mmol), ethyl cyanoacetate (1 mmol), dimedone (1 mmol), ammonium acetate (1.2 mmol) and 0.6 mol % of ILOS@Fe/TSPP were added in a flask and the mixture was magnetically stirred at 75 °C. The reaction progress was monitored by TLC. After the reaction was completed, hot ethanol (10 mL) was added and the obtained mixture was hotly filtered and washed with ethanol. The recovered ILOS@Fe/TSPP catalyst was then reused under optimized conditions for at least 11 times and gave corresponding product in high yield.

2.4. General procedure for the hot filtration test in the preparation of polyhydroquinolines using ILOS@Fe/TSPP catalyst

To do this, benzaldehyde (1 mmol) dimedone (1 mmol), ammonium acetate (1.2 mmol) ethyl acetoacetate (1 mmol) and ILOS@Fe/TSPP (0.6 mol %) were added in a flask with stirring at 75

°C. After ~50% of the coupling reaction was completed, it was stopped and hot ethanol (10 mL) was added and the obtained solution was hotly filtered. The solvent was evaporated and the catalyst free filtrate was then allowed to continue under conditions as before. After 1 h, only a trace conversion of the starting materials was observed.

3.5. The IR, ¹H-NMR and ¹³C-NMR data of some polyhydroquinoline products

Ethyl-4-(2-methylphenyl)-2,7,7-trimethyl--5-oxo--1,4,6,6,8,8-hexahydroquinoline-3-carboxylat:

IR (KBr, cm⁻¹): 3303.4 (NH, stretching vibration), 3078 (C-H, sp² stretching vibration), 2967 (C-H, sp³ stretching vibration), 1697 (C=O, ester), 1637 (C=O, ketone), 1525 (C=C, Ar), 1376, 1315 (C-H, sp³ bending vibration), 1278 (C-O, ether), 757 (*ortho* substitution).

¹H-NMR (400 MHz: DMSO-d₆, 25 °C): δ= 0.81 (s, 3H), 0.98 (s, 3H), 1.1 (t, 3H, J=7.2), 1.92 (d, 1H, J=16), 2.15 (d, 1H, J=16), 2.25-2.35 (m, 4H), 2.43 (d, 1H, J=16), 2.62 (s, 1H), 3.97 (q, 2H, J=7.2), 4.93(s, 1H), 6.85-6.95 (m, 2H), 7.03 (d of d, 1H, J₁=6.4, J₂=2.4), 7.12 (d, 1H J=8), 9.02 (s, 1H).

¹³C-NMR (100 MHz, DMSO-d₆, 25 °C): δ= 14.5, 18.9, 19.8, 26.7, 26.7, 29.5, 32.4, 39.5, 50.7, 59.5, 105.6, 111.9, 126.3, 125.9, 129, 129.6, 135.2, 144.7, 148.1, 149.5, 167.5 (C=O, ester), 194.8 (C=O, ketone).

Ethyl-4-(5-bromo-2-hydroxyphenyl)-2,7,7-trimethyl--5-oxo-1,4,6,6,8,8-hexahydroquinoline-3-carboxylat:

IR (KBr, cm^{-1}): 3318, 3253 (OH, NH, stretching vibrations), 3091 (C-H, sp^2 stretching vibration), 2962 (C-H, sp^3 stretching vibration), 1702 (C=O, ester), 1650 (C=O, ketone), 1590 (C=C, Ar), 1369, 1315 (C-H, sp^3 bending vibration), 1265 (C-O, ether), 543 (C-Br).

^1H -NMR (400 MHz: DMSO-d_6 , 25 $^\circ\text{C}$): δ = 0.86 (s, 3H), 1 (s, 3H), 1.1 (t, 3H, J =7.8), 2.06 (d, 1H, J =16), 2.25 (d, 1H, J =16), 2.25-2.35 (m, 4H), 2.45 (d, 1H, J =16), 3.95 (q, 2H, J =7.8), 4.92 (s, 1H), 6.67 (d, 1H, J =8.4), 7.01 (d, 1H, J =8), 7.17 (d of d, 1H, J_1 =8.4, J_2 =2.6), 9.31 (s, 1H), 9.62 (s, 1H).

^{13}C -NMR (100 MHz, DMSO-d_6 , 25 $^\circ\text{C}$): δ =14.3, 18.63, 26.6, 29.3, 32.1, 32.5, 39.5, 50.2, 59.63, 103.6, 108.9, 110.8, 119.29, 130.1, 136.6, 145.6, 152.3, 152.4, 154.05, 167.1 (C=O ester), 196.6 (C=O ketone).

Methyl-4-isopropyl-2,7,7-trimethyl-5-oxo-1,4,6,6,8,8-hexahydroquinoline-3-carboxylat:

IR (KBr, cm^{-1}): 3293 (NH, stretching vibration), 3073 (C-H, sp^2 stretching vibration), 2954, 2869 (C-H, sp^3 stretching vibration), 1695 (C=O, ester), 1623 (C=O, ketone), 1482 (C=C, Ar), 1376 (C-H, sp^3 bending vibration), 1224 (C-O, ether).

^1H -NMR (400 MHz: DMSO-d_6 , 25 $^\circ\text{C}$): δ = 0.65 (s, 3H), δ = 0.7 (s, 3H), 0.95 (s, 3H), 1.06 (s, 3H), 1.45-1.55 (m, 1H), 2.1 (d, 1H, J =16), 2.17 (d, 1H, J =16), 2.2 (s, 3H), 2.28-2.32 (m, 2H), 3.6 (s, 3H), 3.8 (d, 1H, J =4.4), 8.9 (s, 1H).

^{13}C -NMR (100 MHz, DMSO , 25 $^\circ\text{C}$): δ =18.5, 18.8, 19.1, 27.02, 28.5, 32.2, 35.1, 35.5, 39.5, 50.7, 50.7, 101.5, 108.1, 168.7 (C=O, ester), 195.3 (C=O, ketone).

3. Results and Discussion

Ionic liquid based organosilica (ILOS) was prepared by simultaneous hydrolysis and condensation of 1,3-bis(trimethoxysilylpropyl) imidazolium chloride under acidic conditions [31]. Iron/*meso*-tetrakis(4-sulfonatophenyl)porphyrin (Fe/TSPP) complex was synthesized by sulfonation of the tetraphenyl porphyrin (TPP) with concentrated H₂SO₄ followed by treatment with iron acetate [34]. Ionic liquid based organosilica supported Fe/TSPP complex (ILOS@Fe/TSPP) was then prepared by treatment of Fe/TSPP with ILOS in distilled water according to Scheme 1. The ILO@Fe/TSPP catalyst was characterized with several techniques such as thermal gravimetric analysis (TGA), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM).

Figure 1 shows the steps for the preparation of the ILOS@Fe/TSPP catalyst. Firstly, the Fe/TSPP complex was dissolved in distilled water to give a uniform amethystine solution (Figure 1a). ILOS was also added in water and stirred to give a homogeneously dispersed white powder (Figure 1b). Then, the Fe/TSPP solution was added to the ILOS while stirring. In this step, a light brown mixture was observed (Figure 1c). After that, the obtained mixture was filtered and washed completely with water to remove unsupported Fe/TSPP complex. Finally, the obtained material was dried at 70 °C to give a light brown powder called ILOS@Fe/TSPP (Figure 1d). The presence of organic functional groups (ionic liquid and TSPP moieties) in the material network was confirmed by DRIFT spectroscopy (Figure 2). The DRIFT spectrum of TSPP showed four strong bands at 1218, 1188, 1125 and 1039 cm⁻¹ corresponding to sulfonate groups [34]. This also illustrated four bands at 1555, 1618, 2955 and 3055 cm⁻¹ that can be assigned,

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4 respectively, to C=C, C=N, aliphatic C-H and aromatic C-H bonds (Figure 2a). The DRIFT
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6 spectrum of the ILOS showed three strong bands at 947, 1089, and 1147 cm^{-1} corresponding to
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8 asymmetric and symmetric stretching vibrations of Si-O-Si bonds (Figure 2b) [31, 32]. In
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10 addition, the absorption peaks at 1555 cm^{-1} and 1620 cm^{-1} can be assigned, respectively, to C=C
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12 and C=N bonds of imidazolium ring [31, 32]. The absorption bands of unsaturated C-H
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14 stretching, C-H stretching of propyl moieties of ionic liquids, C-H deformation vibrations, and
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16 C-Si stretching vibrations were observed, respectively, at 3114, 2930, 1455 and 795 cm^{-1} [31,
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18 32]. The broad peak appearing at 3200–3500 cm^{-1} was also due to the stretching vibration of OH
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20 bonds. For ILOS@Fe/TSSP, the abovementioned peaks of both ILOS and Fe/TSSP samples
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22 were observed. Interestingly, for the latter one the intensity of the C-H bands of aromatic rings
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24 (3115 cm^{-1}) was increased. These data confirm successful inclusion and/or immobilization of
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26 ionic liquid and TSSP complex into/onto material framework.
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33 The scanning electron microscopy (SEM) analysis of the ILOS@Fe/TSPP catalyst was also
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35 performed to study the morphology of the material (Figure 3). This image illustrated the
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37 presence of uniform and regular spherical particles. These spherical particles would be good
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39 candidates for chromatography, catalysis, and microelectronics applications due to their high
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41 uniformity and density [35].
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48 Thermal gravimetric analysis (TGA) of the ILOS@Fe/TSPP was carried out from room
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50 temperature to 800 $^{\circ}\text{C}$ to study thermal stability of the material (Figure 4). This analysis
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52 illustrated a weight loss of about 5 % in the temperature below 120 $^{\circ}\text{C}$ corresponding
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54 to removal of water and alcoholic solvents. The second weight loss (15 %) between 300
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56 and 330 $^{\circ}\text{C}$ is assigned to decomposition and elimination of *meso*-tetrakis(4-
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4 sulfonatophenyl)porphyrin moieties confirming successful immobilization of Fe/TSPP
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6 complexes on material surface. The third and main weight loss (31 %) from 330 to 800
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8 °C corresponding to alkyl imidazolium ionic liquid functional groups incorporated in the
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10 material framework. These data are in good agreement with DRIFT spectroscopy and
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12 strongly confirm high thermal stability of the catalyst.
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19 Energy-dispersive X-ray (EDX) spectroscopy of the ILOS@Fe/TSPP was also carried out to
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21 study the presence of expected elements in the material framework (Figure 5). The elemental
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23 distribution mapping of this analysis showed signals of carbon, oxygen, silicon, chlorine,
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25 nitrogen, sulfur and iron in the material. Especially, the presence of Fe and S signals successfully
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27 proves well immobilization of the iron/porphyrin complex on the organosilica material.
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31 The transmission electron microscopy (TEM) image of the ILOS@Fe/TSPP catalyst showed the
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33 presence of spherical particles with average size of 70 nm (Figure 6). This image also illustrated
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35 nano-spaces between the particles which are very good places for successful immobilization and
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37 adsorption of different chemical compounds. The X-ray diffraction (XRD) analysis also
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39 demonstrated a broad peak between 2 theta of 20-40 degree that is characteristic of well-
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41 organized organosilica materials (Figure 7) [36].
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47 After successful characterization, the catalytic activity of ILOS@Fe/TSPP in the Hantzsch
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49 synthesis of polyhydroquinolines was investigated (Table 1). The results illustrated that the
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51 reaction progress is highly affected with temperature, solvent and catalyst loading. As shown,
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53 with increasing the catalyst loading from 0.2 to 0.6 mol %, the yield was significantly increased
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55 (Table 1, entries 1-3) and the best result was obtained in the presence of 0.6 mol % of catalyst. It
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57 is important to note that in the presence of 0.8 mol % of ILOS@Fe/TSPP the same result as 0.6
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mol% was observed (Table 1, entry 4), while increasing the catalyst loading to 1 and 2 mol% resulted a slight decrease in product yield (Table 1, entries 5, 6). With increasing temperature from room temperature to 75 °C, a dominant increase in the yield was observed (Table 1, entries 3, 7, 8). At 85 °C also an excellent yield was obtained, while at 100 °C a decrease in the product amount was observed (Table 1, entries 9, 10). The last result may be attributed to production of side products at elevated temperatures. The efficiency of the catalyst was also considerably affected by solvent (Table 1). Toluene delivered low yield of corresponding product, while CH₃CN, EtOH and H₂O solvents resulted in moderate yield of product using 0.6 mol% of catalyst at 75 °C. Interestingly, under solvent-free media an excellent yield was delivered at the same reaction condition as above (Table 1, entry 3 vs. entries 11-14). To show the neat effect of the supported Fe/TSPP complex in the catalytic process, in the next step the catalytic performance of ILOS was checked under the same condition as before. This material was very sluggish and gave only 8% yield of Hantzsch product, confirming that the catalytic activity mainly resulted from supported iron complex (Table 1, entry 3 vs. entry 15). According to these studies, the use of 0.6 mol% of ILOS@Fe/TSPP catalyst under solvent-free media at 75 °C was selected as optimum condition.

Under these condition, the activity of the catalyst was then investigated in the Hantzsch reaction of a number of aldehyde substrates with alkyl acetoacetates, ammonium acetate and dimedone (Table 2). As shown, benzaldehyde and other aromatic aldehydes furnished the polyhydroquinoline derivatives in high to excellent yields. Clearly, the effect of the nature of the substituent on the aromatic ring showed no significant effect on this conversion, because they were delivered in excellent yields. As shown, electron-withdrawing groups containing aromatic aldehydes such as 4-nitrobenzaldehyde (Table 2, entry 2), 3-nitrobenzaldehyde (Table 2, entry

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4 3), 2-chlorobenzaldehyde (Table 2, entry 4), 4-chlorobenzaldehyde (Table 2, entries 5, 6), 3-
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6 bromobenzaldehyde (Table 2, entries 7, 8) gave excellent yields of polyhydroquinoline products
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8 at very short time. Furthermore, aromatic aldehydes bearing electron-donating groups such as 5-
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10 bromo-2-hydroxy-benzaldehyde (Table 2, entry 9), 2-methylbenzaldehyde (Table 2, entry 10), 4-
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12 methylbenzaldehyde (Table 2, entries 11, 12) and 4-methoxybenzaldehyde (Table 3, entries 13,
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14 14) also afforded high yields of the corresponding coupling adducts at 10-15 minutes under the
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16 same reaction condition as above. It is also worth noting that more sterically demanding
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18 substrates were also converted to the corresponding products as exemplified by entries 4 and 10
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20 of Table 2. Moreover, the aliphatic aldehydes, which are usually less reactive substrates in
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22 organic transformations, were also smoothly converted to their corresponding products (Table 2,
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24 entry 15). These results demonstrate the high performance of the designed catalyst for the
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26 preparation of a wide range of polyhydroquinoline derivatives applicable in areas of drug design
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28 and fine chemical.
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36 Since the recoverability and reusability of the catalyst are very important issues, especially in the
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38 case of solid catalysts, in the next step the reusability of the designed catalyst was investigated
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40 under optimized reaction condition in the condensation of benzaldehyde with dimedone,
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42 ammonium acetate and ethylacetoacetate. This study illustrated that the catalyst could be
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44 recovered at least 11 times without significant decrease in efficiency (Figure 8).
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48 Although, according to reusability test no significant decrease in the efficiency of the catalyst
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50 was observed, to test if any iron/TSPP complex is leached from the ILOS surface during the
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52 process, a hot filtration test was next performed in the reaction of benzaldehyde with dimedone,
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54 ammonium acetate and ethyl acetoacetate, after ~50% of the coupling reaction was completed.
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56 Interestingly, we found that only a trace conversion (<4%) of the coupling reaction was observed
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upon the heating of the catalyst-free solution for 1 h at 75 °C. Moreover, no iron species were detected by using atomic absorption spectroscopy analysis on filtrate. These observations significantly prove high recoverability, reusability, reactivity and stability of the present catalyst under applied reaction conditions. The high stability and durability of the catalyst may be attributed to effective electrostatic interactions between Fe/TSPP anions and incorporated ionic liquid cations that protect catalytic Fe-complexes against leaching and deactivation (Scheme 1).

4. Conclusion

In conclusion, for the first time, a novel ionic liquid based organosilica supported Fe/TSPP complex (ILOS@Fe/TSPP) was prepared, characterized and its catalytic application was successfully developed in the synthesis of polyhydroquinolines. The DRIFT, EDX and TG analyses of the ILOS@Fe/TSPP confirmed well immobilization and excellent stability of the ionic liquid and Fe/TSPP moieties in the material network. The ILOS@Fe/TSPP was successfully applied in the one-pot condensation of aldehydes with alkyl acetoacetates, ammonium acetate and dimedone to give corresponding Hantzsch products in high to excellent yields. This catalyst was easily recovered and reused at least 11 times without significant decrease in efficiency. Some other advantages of this study are solvent-free media, very short reaction times, high yield of products as well as high activity, stability and durability of the catalyst during applied reaction conditions. According to aforementioned properties of this catalytic system, some of its applications in the other chemical processes are underway in our laboratories.

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Table 1. The effect of solvent and catalyst loading in the Hantzsch reaction^a

Entry	Catalyst	Catalyst (mol %)	T (°C)	Solvent	Yield (%) ^b
1	ILOS@Fe/TSPP	0.2	75	-	35
2	ILOS@Fe/TSPP	0.4	75	-	68
3	ILOS@Fe/TSPP	0.6	75	-	95
4	ILOS@Fe/TSPP	0.8	75	-	96
5	ILOS@Fe/TSPP	1	75	-	93
6	ILOS@Fe/TSPP	2	75	-	90
7	ILOS@Fe/TSPP	0.6	25	-	38
8	ILOS@Fe/TSPP	0.6	50	-	65
9	ILOS@Fe/TSPP	0.6	85	-	96
10	ILOS@Fe/TSPP	0.6	100	-	88
11	ILOS@Fe/TSPP	0.6	75	Toluene	23
12	ILOS@Fe/TSPP	0.6	75	EtOH	57
13	ILOS@Fe/TSPP	0.6	75	CH ₃ CN	45
14	ILOS@Fe/TSPP	0.6	75	H ₂ O	50
15	ILOS	- ^c	75	-	8

^a Reaction conditions: Benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), dimedone (1 mmol), ammonium acetate (1.2 mmol), 15 min. ^b Isolated yields. ^c The amount of ILOS was the same as used ILOS@Fe/TSPP.

Table 2. Preparation of polyhydroquinolines in the presence of ILOS@Fe/TSP catalyst under solvent free condition^a

Entry	R ₁	R ₂	Time (min)	Yield (%) ^b	TON ^c	M. P. (°C)
1	C ₆ H ₅	OEt	15	96	160	203-205
2	4-NO ₂ C ₆ H ₄	OEt	5	95	158.5	244-245
3	3-NO ₂ C ₆ H ₄	OMe	10	92	154	235-237
4	2-ClC ₆ H ₄	OMe	15	86	144	209-211
5	4-ClC ₆ H ₄	OMe	7	94	157	246-247
6	4-ClC ₆ H ₄	OEt	7	95	158.5	245-247
7	3-BrC ₆ H ₄	OEt	12	88	147	232-234
8	3-BrC ₆ H ₄	OMe	12	90	150	225-226
9	5-Br-2-OH-C ₆ H ₄	OEt	10	90	150	234-236
10	2-CH ₃ C ₆ H ₄	OEt	15	88	147	212-214
11	4-CH ₃ C ₆ H ₄	OEt	10	97	162	260-262
12	4-CH ₃ C ₆ H ₄	OMe	10	92	154	265-268
13	4-CH ₃ OC ₆ H ₄	OMe	10	97	162	258-260
14	4-CH ₃ OC ₆ H ₄	OEt	10	97	162	255-256
15	(CH ₃) ₂ CHCHO	OMe	20	80	134	198-200

^a Conditions: Aldehyde (1 mmol), dimedone (1 mmol), methyl/ethylacetoacetate (1 mmol), ammonium acetate (1.2 mmol) and catalyst (0.6 mol %). ^bIsolated yield. ^cTON = Turnover number (defined as mmol of product/mmol of catalyst).

Scheme and Figure captions:

Scheme 1. Preparation of the ILOS@Fe/TSPP catalyst and its application in the synthesis of polyhydroquinolines

Figure 1. Steps for the preparation of the ILOS@Fe/TSPP catalyst: a) aqueous solution of Fe/TSPP, b) uniform distribution of ILOS in water, c) mixing and stirring of a and b at room temperature, d) ILOS@Fe/TSPP powder.

Figure 2. DRIFT spectra of a) Fe/TSPP, b) ILOS, and c) ILOS@Fe/TSPP

Figure 3. SEM image of the ILOS@Fe/TSPP catalyst

Figure 4. Thermal gravimetric analysis of the ILOS@Fe/TSPP catalyst

Figure 5. Energy-dispersive X-ray (EDX) spectroscopy of the ILOS@Fe/TSPP catalyst

Figure 6. Transmission electron microscopy (TEM) image of the ILOS@Fe/TSPP catalyst

Figure 7. X-ray diffraction analysis of the ILOS@Fe/TSPP catalyst

Figure 8. Reusability of the ILOS@Fe/TSPP catalyst

Scheme 1

Figure 1

Figure 2

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Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Graphical abstract

An ionic liquid based organosilica supported Fe/porphyrin catalyst is applied in the Hantzsch reaction.