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Preparation of Iron-Containing Schiff Base and Ionic Liquid Based Bifunctional Periodic Mesoporous Organosilica and Its Application in the Synthesis of 3,4-Dihydropyrimidinones

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A novel iron-containing Schiff base and ionic liquid based bifunctional periodic mesoporous organosilica (Fe@SBIL-BPMO) was prepared, characterized, and its catalytic application was developed. The SBIL-BPMO was first prepared by the grafting of 3-aminopropyltrimethoxysilane on an ionic-liquid-based PMO followed by treatment with 2-hydroxybenzaldehyde in toluene at reflux. This material was then reacted with $Fe(NO_3)_3 \cdot 9H_2O$ to afford the Fe@BPMO-SBIL nanocatalyst. The catalyst was characterized by thermogravimetric analysis, nitrogen sorption experiments, diffuse reflectance FTIR spectroscopy, low-angle powder XRD, and TEM. The Fe@SBIL-BPMO catalyst was successfully applied in the one-pot synthesis of 3,4-dihydropyrimidinone/thione derivatives under solvent-free reactions. The stability, reactivity, and reusability of the catalyst under the reaction conditions have also been investigated.

Introduction

The metal-catalyzed synthesis of 3,4-dihydropyrimidinones/thiones through the Biginelli reaction is an important and valuable chemical process that is of particular interest owing to its key role in the production of drugs applicable in different areas of pharmacology.[1,2] Some pharmaceutical properties of these compounds include anticancer, anti-HIV, calcium channel modulator, antihypertensive, antitumor, antibacterial, antioxidant, and antiviral activities.[3] Traditionally, the Biginelli reaction was performed under homogeneous conditions in the presence of many metal-based Lewis acid catalysts. Some improved catalysts include $La(OTf)_3$ (OTf = triflate), $ZnCl_2$, $ZnBr_2$, $CuCl_2$, $NiCl_2$, ZnI_2, VCl_3, $LiClO_4$, $Sr(OTf)_2$, $BF_3 \cdot OEt_2$, $FeCl_3$, $LaCl_3$, InX_3 (X = Cl, Br), $BiCl_3$, $Yb(OTf)_3$, $ZrCl_4$, $Mn(OAc)_3$, $Cu(OTf)_2$, $Cu(OAc)_2$, $LaCl_3$–graphite, LiBr, GaX_3, and $[bmim][FeCl_4]$ (bmim = 1-butyl-3-methylimidazolium).[1,2] However, because these homogeneous catalytic systems are usually expensive, toxic, and require large amounts of unrecoverable catalyst, on the basis of economic criteria and toxicological concerns, it is more desirable to reduce the amounts of metal-based catalyst used in potential chemical processes. To overcome these restrictions, several improvements were recently attempted by immobilization or supporting metal catalysts on different reusable and recoverable surfaces such as silica, alumina, polymers, and resin.[4] Nevertheless, some of these processes suffer from environmental pollution caused by the utilization of organic solvents, exotic reaction conditions, long reaction times, and most importantly high loading and leaching of the catalyst during the reaction. Accordingly, the development of efficient and environmentally friendly metal-based catalytic systems that are easily prepared, recoverable, and reusable is still needed for the Biginelli reaction.

On the other hand, metal-containing hybrid organic–inorganic materials are a significant topic that has attracted much attention from chemists owing to the metal possessing excellent catalytic activity and the possibility of easy recovery and reuse.[5] The preparation of these materials is achieved by the impregnation of metallic complexes with supports containing a suitable ligand and/or by simultaneous cocondensation of a metal–ligand complex with a hydrolysable and condensable organic/inorganic precursor under acidic or basic conditions.[5] In particular, metal-containing ordered mesoporous organosilica (M@OMO) materials are more interesting owing to advantages of high surface area, easy diffusion of organic substrates for typical transformations, as well as high thermal and mechanical stability.[6] A valuable achievement in this area is the creation and applications of the periodic mesoporous organosilica-supported metal catalyst (M@PMO) with excellent stability of the catalytic centers and organic moieties.[7] Accordingly, several M@PMO materials have been recently prepared and their catalytic applications have been successfully applied in a number of organic transformations.[7–10] For example, recently we prepared and developed some metal-containing periodic mesoporous organosilicas with an ionic-liquid framework (M@PMO-IL; M = Pd, Ru, Cu, Mn, WO_4^{2-}) and studied their applications in oxidation and cross-coupling reactions.[10] Our studies demonstrated that PMO-IL was a powerful and highly

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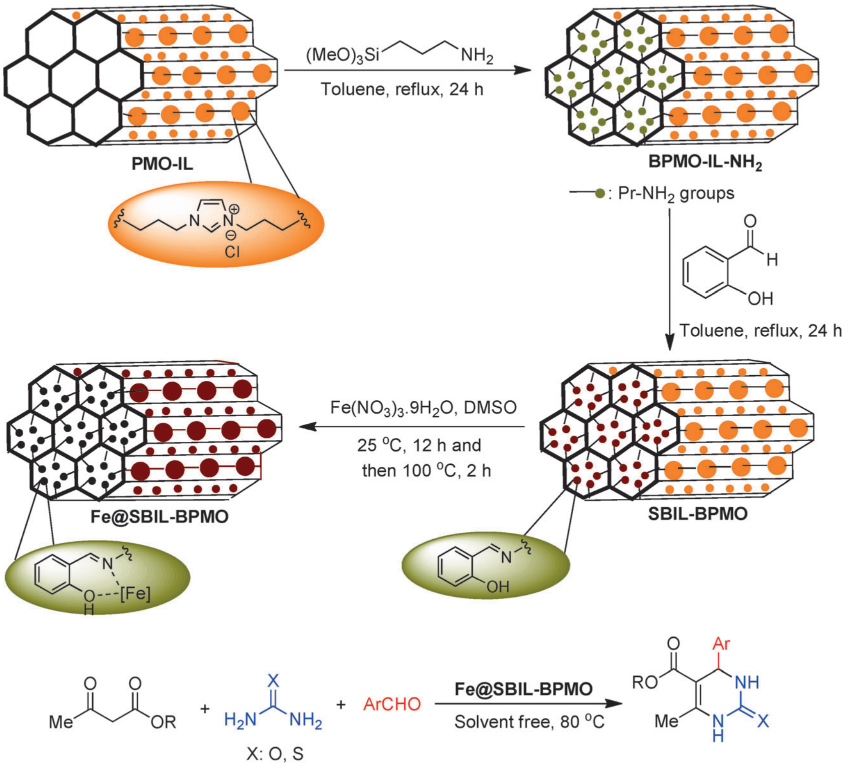


Scheme 1. Preparation of the Fe@SBIL-BPMO nanocatalyst and its application in the synthesis of 3,4-dihydropyrimidinones/thiones.

stable support for metal complexes and could be recovered several times with retention of efficiency. As a continuation of these studies, herein we wish to disclose a protocol for the preparation a novel iron-containing Schiff base and ionic liquid based bifunctional PMO (Fe@SBIL-BPMO) nanocatalyst and a study on its performance in the one-pot, three-component Biginelli condensation of aldehydes, urea/thiourea, and alkyl acetoacetate (Scheme 1). The effect of the SBIL-BPMO support on the immobilization, stabilization, and reactivity of metallic catalytic sites during the reaction process has also been investigated.

Results and Discussion

The preparation of Fe@SBIL-BPMO was achieved by immobilization of $Fe(NO_3)_3{\cdot}9H_2O$ on a novel BPMO material. First, the ionic-liquid-based periodic mesoporous organosilica (PMO-IL) was prepared according to our previous procedure.[10] This was then reacted with 3-aminopropyltrimethoxy silane by a grafting approach to give the aminopropyl-functionalized PMO nanomaterial (PMO-IL-NH_2). Next, PMO-IL-NH_2 was treated with 2-hydroxybenzaldehyde in toluene at reflux to produce Schiff base and ionic liquid based bifunctional PMO (SBIL-BPMO). Finally, Fe@SBIL-BPMO was obtained by treatment of SBIL-BPMO with a substoichiometric amount of $Fe(NO_3)_3{\cdot}9H_2O$ (Scheme 1). This catalyst was characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), thermogravimetric analysis (TGA), nitrogen-sorption experiments, low-angle powder X-ray diffraction (LAPXRD), and TEM. The nitrogen adsorption–desorption analysis of all PMO-IL, SBIL-BPMO, and Fe@SBIL-BPMO samples exhibited type IV isotherms with clear H1 hysteresis loops at high relative pressures and a vertical capillary condensation step at $P/P_0 \approx 0.7–0.8$; this indicated that the materials had very regular mesochannels, which is a characteristic of large-pore mesoporous materials with a uniform 2D hexagonal structure (Figure 1). In addition, all samples possessed narrow BJH pore size distributions; however, for SBIL-BPMO and Fe@SBIL-BPMO the pore size of the mesostructure decreased from 10.5 to 9.3 nm. Moreover, after functionalization with *ortho*-hydroxybenzaldehyde, followed by treatment with the iron complex, the BET surface area and

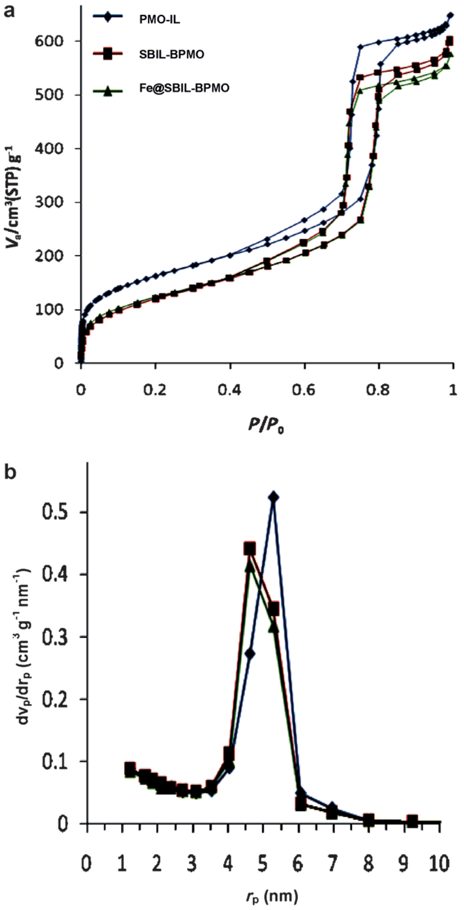


Figure 1. Nitrogen adsorption–desorption (a) and Barrett–Joyner–Halenda (BJH) pore size distribution (b) isotherms of the PMO-IL, SBIL-BPMO, and Fe@SBIL-BPMO nanomaterials.

pore volume decreased in the order of PMO-IL > SBIL-BPMO > Fe@SBIL-BPMO (Table 1), but the isotherm pattern remained unchanged. These results confirm the successful immobilization of the *ortho*-hydroxybenzaldehyde ligand and iron complex inside the channels of the mesoporous PMO-IL material without disturbing its periodic nature. TEM analysis and LAPXRD of the Fe@SBIL-BPMO catalyst were next performed to verify the periodicity of the pores. According to the TEM image, when the electron beam was introduced perpendicularly to the channel axis, a parallel alignment of channels was observed (Figure 2), whereas hexagonal packing of the cylindrical mesopore was revealed when the electron beam was introduced along the channel axis (Figure 2, inset). The LAPXRD results for the catalyst also illustrated a diffraction peak with high intensity at $2\theta = 0.9°$, which was indexed to the $d100$ reflection (Figure 3). The $d110$ and $d200$ reflections were also observed at $2\theta = 1.5$ and $1.7°$, respectively; this confirmed that the material possessed a highly ordered hexagonal mesostructure. Moreover, these analyses together with the results from nitrogen-sorption experiments showed that, after loading of 2-hydroxybenzalehyde and the iron complex, the structural integrity and order of the mesochannels were maintained, which proved the high mechanical stability of the material.

Table 1. Structural parameters of PMO-IL, SBIL-BPMO, and Fe@SBIL-BPMO materials determined from nitrogen-sorption experiments.

Sample	BET surface area [$m^2 g^{-1}$]	Pore diameter [nm]	Pore volume [$cm^3 g^{-1}$]
PMO-IL	645	10.5	1.15
SBIL-BPMO	518	9.3	0.93
Fe@SBIL-BPMO	478	9.3	0.82

TGA of Fe@SBIL-BPMO was also performed to validate the thermal stability of the catalyst. This analysis was performed from room temperature to 800 °C (Figure 4), and revealed three weight losses at different temperature ranges. The first one from 10 to 110 °C (6.04 %) is attributed to removal of water and alcoholic solvents remaining from the synthetic process. The second one between 110 and 300 °C (5.07 %) corresponds to elimination of the surfactant template remaining from the synthetic process. The main weight loss appearing between 301 and 800 °C (24.45 %) is related to propyl Schiff base and ionic-liquid groups located in the surface and body of the material network. These data prove the high thermal stability of the material.

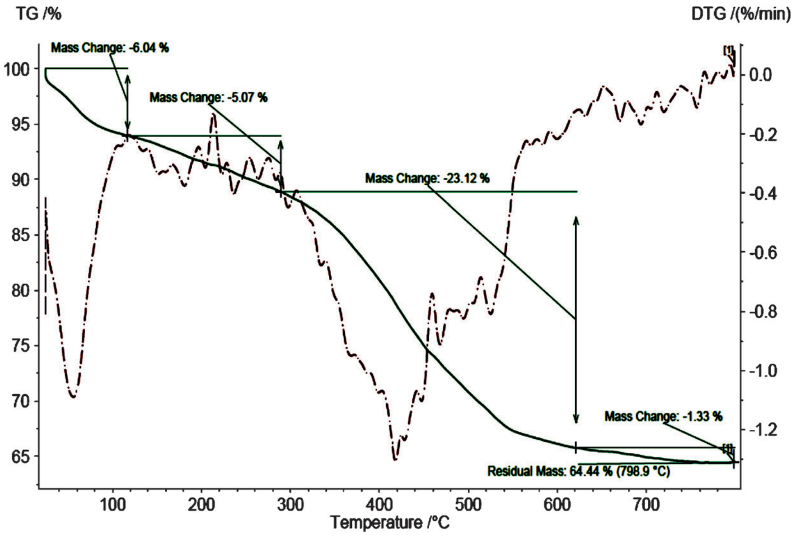


Figure 4. TGA results for the Fe@SBIL-BPMO nanocatalyst.

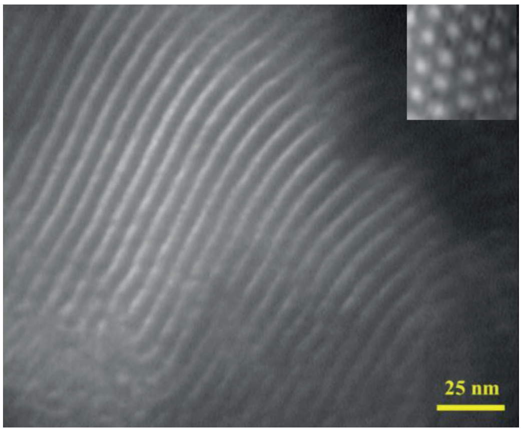


Figure 2. TEM image of the Fe@SBIL-BPMO nanocatalyst.

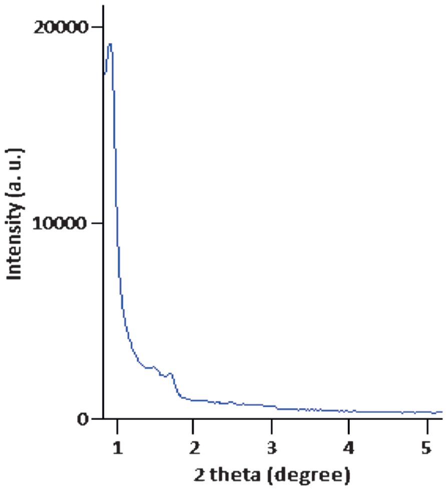


Figure 3. LAPXRD results for the Fe@SBIL-BPMO catalyst.

The presence of organic functional groups in the material network was confirmed by DRIFTS (Figure 5). The strong bands at $\tilde{\nu} = 1145$, 1076, and 956 cm^{-1} are attributed to asymmetric

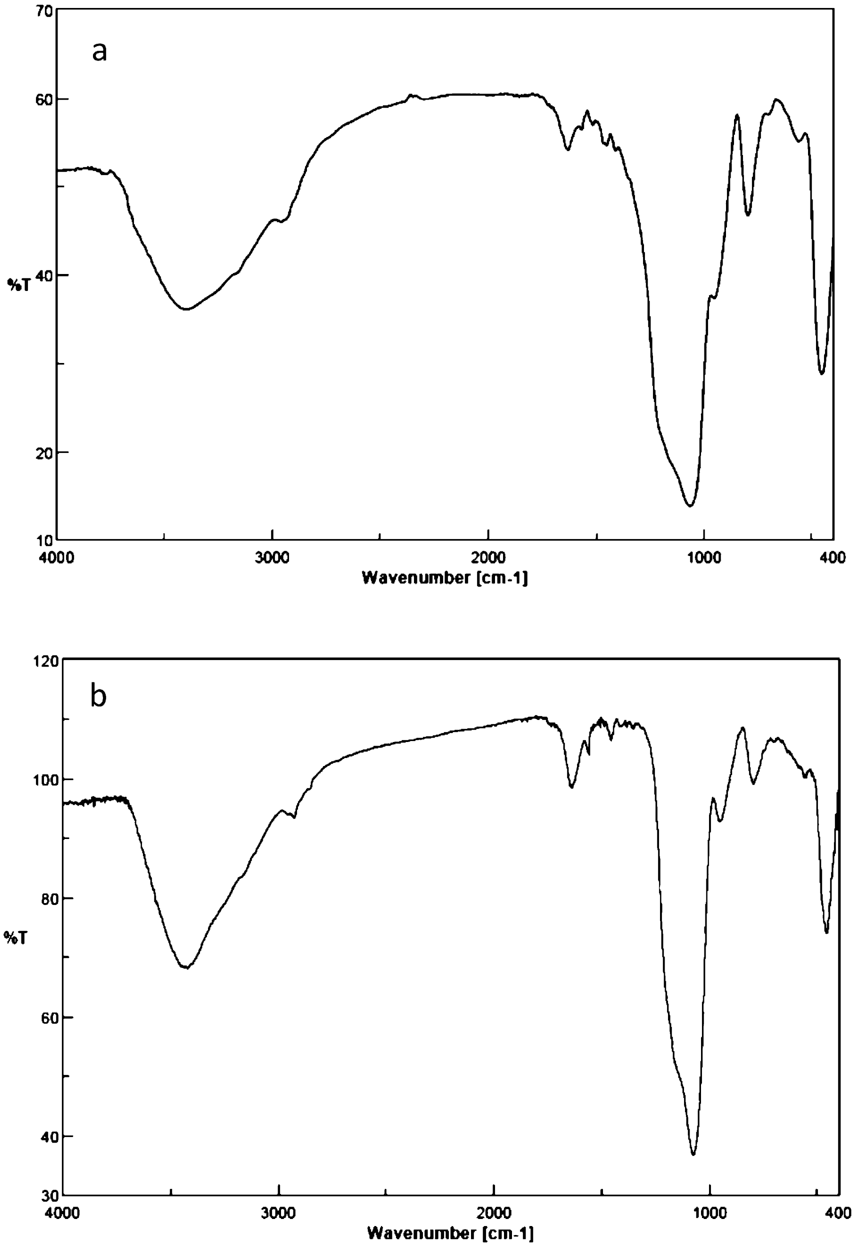


Figure 5. DRIFTS results for the PMO-IL (a) and Fe@SBIL-BPMO (b) nanomaterials.

and symmetric stretching vibrations of Si–O–Si bonds.[10c] In addition, the strong and broad band appearing at $\tilde{\nu} = 3200$–$3500\ \text{cm}^{-1}$ is due to the stretching vibration of O–H bonds. Moreover, the absorption bands of organic functional groups are observed at $\tilde{\nu} = 3125$ (for unsaturated C–H stretching), 2927 and 2855 (C–H stretching of aliphatic moieties), 1637 (C=N stretching of Schiff base and imidazolium ring),[4g, 10c] 1457 (C–H deformation vibrations), 797 (for C–Si stretching vibrations), and $455\ \text{cm}^{-1}$ (bending vibration of Si–O–Si). Interestingly, for Fe@SBIL-BPMO, the intensity of the C=N band ($\tilde{\nu} = 1637\ \text{cm}^{-1}$) is increased, which proves that the 2-hydroxybenzaldehyde functional group is chemically bound in the mesochannels of PMO-IL.[4g] These data are in good agreement with TGA results and confirm the successful inclusion and immobilization of alkyl imidazolium ionic liquid and Schiff base groups in the material framework.

After characterization, the performance of the Fe@SBIL-BPMO nanocatalyst was investigated in the one-pot, three-component condensation of benzaldehyde, methyl acetoacetate, and urea as a test model (Table 2). In the first study, the effect of solvent was studied: in toluene, a low yield was obtained, whereas in H_2O, EtOH, and CH_3CN a moderate yield of the desired coupling product was obtained (Table 2, entries 1–4). This may be attributed to the low solubility of the starting materials in the toluene. Importantly, under solvent-free media, a quantitative yield of product was obtained (Table 2, entry 5). The reaction was also affected by the catalyst loading and the best result was observed in the presence of 0.8 mol% of catalyst (Table 2, entries 5–7). The reaction progress was also strongly affected by temperature. The reaction was very slow and gave low to moderate yields of the product at 30 and 60 °C, but was accelerated with increasing temperature, and at 80 °C gave quantitative yield (Table 2, entry 5 vs. entries 8 and 9).

With the optimized conditions in hand, the scope and

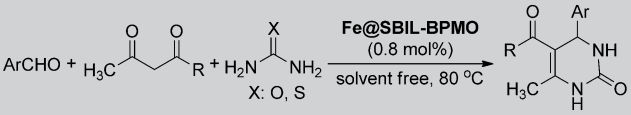
Table 2. The effect of solvent, temperature, and catalyst loading in the Biginelli reaction of benzaldehyde with urea and methyl acetoacetate in the presence of Fe@SBIL-BPMO.[a]

Entry	Catalyst loading [mol%]	T [°C]	Solvent	Yield [%][b]
1	0.8	80	H_2O	58
2	0.8	80	EtOH	68
3	0.8	80	CH_3CN	76
4	0.8	80	toluene	8
5	**0.8**	**80**	–	**97**
6	0.5	80	–	55
7	0.3	80	–	30
8	0.8	60	–	54
9	0.8	30	–	9

[a] Reaction conditions: benzaldehyde (1 mmol), methyl acetoacetate (1 mmol), urea (1.5 mmol), 50 min. [b] Yields of product isolated.

generality of this protocol were then demonstrated by testing a broad range of substrates, and the results showed that the presence of either electron-withdrawing or -donating substituents on the aldehydes did not have a significant effect on their reactivity or product yield. As shown in Table 3, benzaldehyde, with both urea and thiourea, delivered a quantitative yield of the corresponding coupling adducts under the optimized reaction conditions and in short times (Table 3, entries 1–4).

Table 3. Preparation of Biginelli products in the presence of the Fe@SBIL-BPMO nanocatalyst.[a]

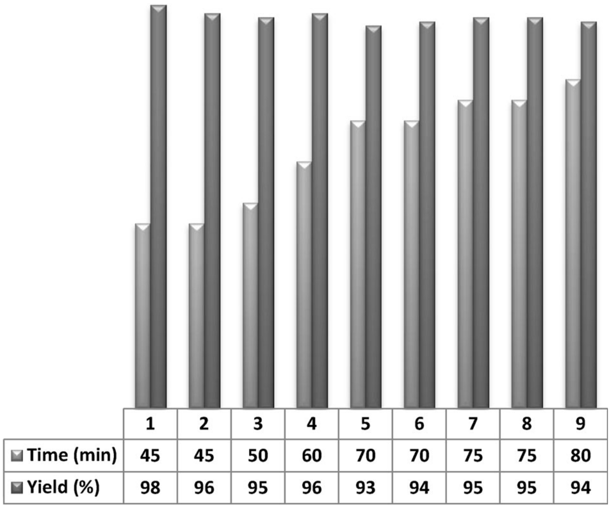


Entry	Ar	R	t [min]	Yield [%][b] (TON)[c]	M.p. [°C]
1	C_6H_5	OMe	50	97 (121.25)	208–212
2	C_6H_5	OEt	50	95 (118.75)	203–206
3	C_6H_5	OMe	65	94 (117.5)	222–224[d]
4	C_6H_5	OEt	65	94 (117.5)	206–207[d]
5	4-$MeOC_6H_4$	OMe	50	95 (118.75)	190–192
6	4-$MeOC_6H_4$	OEt	65	93 (116.25)	148–150[d]
7	4-$CH_3C_6H_4$	OMe	50	95 (118.75)	205–207
8	4-$CH_3C_6H_4$	OEt	50	96 (120)	213–215
9	4-$CH_3C_6H_4$	OEt	65	96 (120)	190–193[d]
10	2-$MeOC_6H_4$	OEt	80	86 (107.5)	257–258
11	3-BrC_6H_4	OMe	55	94 (117.5)	214–217
12	3-BrC_6H_4	OEt	55	93 (116.25)	195–197
13	2-ClC_6H_4	OMe	80	83 (103.75)	251–253
14	2-ClC_6H_4	OEt	80	85 (106.25)	213–215
15	3-ClC_6H_4	OMe	70	91 (113.75)	209–210
16	4-ClC_6H_4	OEt	70	92 (115)	208–211
17	4-CNC_6H_4	OEt	95	85 (106.25)	203–205
18	4-$NO_2C_6H_4$	OMe	120	83 (103.75)	233–235

[a] Reaction conditions: aldehyde (1 mmol), ethyl/methyl acetoacetate (1 mmol), urea/thiourea (1.5 mmol). [b] Yield of products isolated. [c] TON = turnover number (defined as mmol of product/mmol of catalyst). [d] Thiourea was used instead of urea.

Moreover, electron-donating substituents containing aldehydes, such as 4-methoxybenzaldehyde, 4-methylbenzaldehyde, and 2-methoxybenzaldehyde (Table 3, entries 5–10) gave high to excellent yields of the desired products under the optimized conditions. Aromatic aldehydes with electron-withdrawing groups, such as 3-bromobenzaldehyde, 2-chlorobenzaldehyde, 3-chlorobenzaldehyde, 4-chlorobenzaldehyde, 4-cyanobenzaldehyde, and 4-nitrobenzaldehyde, also delivered high yields of the corresponding products (Table 3, entries 11–18). It is also important to note that sterically demanding *ortho*-substituted aromatic aldehydes were used and tolerated high yields of the corresponding products (Table 3, entries 10, 13, and 14). These observations prove the efficiency of the catalyst for the preparation of different derivatives of Biginelli compounds that are important for drug synthesis. To prove whether the catalyst acts hetero- or homogeneously, a standard leaching experiment was conducted for the condensation of benzaldehyde, urea, and methyl acetoacetate as a test model. To do this, the reaction was performed for 30 min under the optimized conditions, then the catalyst was removed by filtration, and the reaction was allowed to proceed without catalyst. There was no change in the yield, even after heating at 80 °C for 120 min; this indicated that no homogeneous catalyst was involved. Moreover, atomic adsorption spectroscopy (AAS) performed for the filtrate showed that the amount of leached iron was less than 1 ppm. These results illustrate that the catalyst may operate in a heterogeneous manner. These observations may be attributed to Schiff base and ionic-liquid ligands, which strongly immobilize active catalytic iron species during the applied reaction conditions and protect them from leaching and deactivation.

Because the reusability of the catalysts is an important benefit and makes them useful for commercial applications, in another experiment the reactivity and reusability of the present catalyst was studied in the reaction of benzaldehyde, methyl acetoacetate, and urea (Figure 6). To determine the recoverability and reusability, after completion of the reaction, the reaction mixture was filtered and washed completely with ethanol to recover the catalyst. The recovered catalyst was dried and then used again in the same reaction; this led to a yield of 96%. Further investigations showed that the catalyst could be recovered and reused at least eight times without any considerable loss in efficiency under the same conditions as those used for the run with fresh catalyst.



	1	2	3	4	5	6	7	8	9
▨ Time (min)	45	45	50	60	70	70	75	75	80
▨ Yield (%)	98	96	95	96	93	94	95	95	94

Figure 6. Recoverability and reusability of the Fe@SBIL-BPMO nanocatalyst.

In addition, the reactivity of the catalyst was also investigated. For this, after completion of the reaction in the first run, fresh substrates were added to the previous reaction mixture in the same flask and stirring was performed to complete the second cycle. These cycles occurred at least 15 times without a noticeable decrease in the catalyst reactivity, although longer reaction times than those used for the first run were required (Table 4). These data strongly confirm the powerful reactivity, reusability, and durability of the catalyst during the applied conditions.

TEM analysis of the recovered catalyst after five cycles was also performed to investigate the stability of the catalyst meso-

Table 4. Reactivity of the Fe@SBIL-BPMO catalyst in the Biginelli reaction of benzaldehyde with methyl acetoacetate and urea.

Run	*t* [min]	Run	*t* [min]	Run	*t* [min]
1	45	6	65	11	80
2	45	7	70	12	80
3	55	8	70	13	80
4	60	9	75	14	85
5	60	10	75	15	90

structure. This showed a pore structure with uniform, regular 2D symmetry that was the same as that of the fresh catalyst (Figure 7). These results are in good agreement with recovery data and successfully confirm the superior structural stability of the catalyst during the reaction conditions.

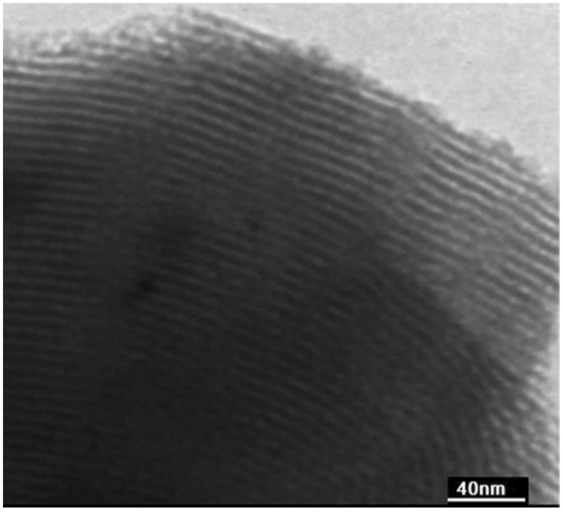


Figure 7. TEM image of the recovered Fe@SBIL-BPMO catalyst after the fifth cycle.

Conclusion

A novel Fe@SBIL-BPMO catalyst was prepared, characterized, and its catalytic performance was developed in the Biginelli reaction. DRIFTS and TGA strongly confirmed the successful incorporation and stabilization of ionic-liquid and Schiff base groups in the material framework. The nitrogen adsorption–desorption analysis, PXRD, and TEM results also showed the presence of a uniform, highly regular 2D structure for the catalyst. This novel nanocatalyst illustrated the high reactivity and selectivity for the preparation of various derivatives of dihydropyrimidinones/thiones through the Biginelli reaction under solvent-free conditions. Moreover, this catalyst was successfully reused and recovered for several consecutive runs, and retained its catalytic efficiency and selectivity. A TEM image of the recovered catalyst confirmed the high structural stability of the material under the applied reaction conditions. Some other advantages of this study were simple workup, easy catalyst recovery, high yields of products, and low catalyst loading. According to the aforementioned advantages, some applications of the catalyst in other chemical processes are underway in our laboratory.

Experimental Section

Preparation of PMO-IL-NH$_2$

First, the PMO-IL material was prepared according to our previously reported procedure.[10] This was then modified with 3-aminopropyltrimethoxyslane through a grafting approach. Typically, PMO-IL (1 g) was added to a flask containing dry toluene (50 mL) at 25 °C and stirred for about 5 min. After complete dispersion of PMO-IL in toluene, 3-aminopropyltrimethoxysilane (0.5 mmol) was added and the mixture was heated at reflux under an argon atmosphere for 24 h.[11] The obtained precipitate was filtered and completely washed with ethanol to remove unreacted aminopropyltrimethoxysilane. The final material was dried for 12 h at 70 °C to give PMO-IL-NH$_2$ as a white powder.

Preparation of SBIL-BPMO

SBIL-BPMO was prepared by the reaction of PMO-IL-NH$_2$ with 2-hydroxybenzaldehyde in toluene at reflux. Typically, PMO-IL-NH$_2$ (1 g) was added to a round-bottomed flask containing dry toluene (50 mL) and stirred at room temperature. After complete dispersion of PMO-IL-NH$_2$, 2-hydroxybenzaldehyde (0.6 mmol) was added and the mixture was heated at reflux for 24 h. The obtained precipitate was then filtered and completely washed with ethanol to remove unreacted 2-hydroxybenzaldehyde. The resulting solid was dried at 70 °C for 12 h to give SBIL-BPMO.

Preparation of Fe@SBIL-BPMO

The Fe@SBIL-BPMO nanocatalyst was prepared by the treatment of SBIL-BPMO with a substoichiometric amount of $Fe(NO_3)_3 \cdot 9H_2O$ in DMSO. SBIL-BPMO (1 g) was added to a flask containing DMSO (5 mL) and stirred at room temperature. After complete dispersion of SBIL-BPMO, $Fe(NO_3)_3 \cdot 9H_2O$ (0.7 mmol) was added and the resulting mixture was stirred at 25 °C for 12 h and then at 100 °C for 2 h. After cooling the reaction solution to room temperature, the obtained mixture was filtered and completely washed with ethanol to remove unsupported $Fe(NO_3)_3 \cdot 9H_2O$. The obtained Fe@SBIL-BPMO powder was next dried at 70 °C for 12 h under vacuum. Elemental analysis showed that the loading of Fe on the solid material was 0.38 mmol Fe per gram.

General procedure for the preparation of Biginelli products by using the Fe@SBIL-BPMO nanocatalyst

For this, Fe@SBIL-BPMO nanocatalyst (0.8 mol %) was added to a flask containing a homogeneous mixture of aldehyde (2 mmol), alkyl acetoacetate (2 mmol), and urea/thiourea (3 mmol). The obtained solution was then magnetically stirred under solvent-free conditions at 80 °C for an appropriate time, as indicated in Table 2. The reaction progress was monitored by TLC. After completion of the reaction, warm ethanol (8 mL) was added and the reaction mixture was separated from the catalyst by filtration and washing with warm ethanol. The filtrate was then placed in an ice bath to precipitate crude crystals. Finally, pure products were obtained after recrystallization in ethanol.

General procedure for the recovery of the Fe@SBIL-BPMO nanocatalyst in the Biginelli reaction

The Fe@SBIL-BPMO nanocatalyst (0.8 mol%) was added to a flask containing a homogeneous solution of aldehyde (5 mmol), alkyl acetoacetate (5 mmol), and urea (7.5 mmol), and the mixture was magnetically stirred at 80 °C. The reaction progress was monitored by TLC. After the reaction was completed, warm ethanol (10 mL) was added and the obtained solution was hot filtered. The catalyst was separated from the reaction mixture by further washing with warm ethanol. This catalyst was reused at least eight times under the same conditions as those used for the first run, and delivered the corresponding 3,4-dihydropyrimidinone product in high yield and selectivity.

General procedure for the reactivity of the Fe@SBIL-BPMO nanocatalyst in the Biginelli reaction

Fe@SBIL-BPMO nanocatalyst (0.8 mol%) was added to a flask containing benzaldehyde (2 mmol), ethyl acetoacetate (2 mmol), and urea (3 mmol), and the mixture was stirred at 80 °C under solvent-free conditions. After completion of the reaction, as monitored by TLC, the starting materials without catalyst (benzaldehyde (2 mmol), ethyl acetoacetate (2 mmol), and urea (2 mmol)) were added and the reaction progress was monitored under the same conditions as those used in the first run (solvent free, 80 °C). After completion of the reaction, the latter process was repeated at least 14 times without a significant decrease in the activity of the catalyst.

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Keywords: ionic liquids · iron · nanostructures · Schiff bases · supported catalysts

[1] a) C. O. Kappe, *Acc. Chem. Res.* **2000**, *33*, 879–888; b) M. Syamala, *Org. Prep. Proced. Int.* **2009**, *41*, 1–68; c) Suresh, J. S. Sandhu, *Arkivoc* **2012**, *i*, 66–133.

[2] a) K. Ananda Kumar, M. Kasthuraiah, C. Suresh Reddy, C. D. Reddy, *Tetrahedron Lett.* **2001**, *42*, 7873–7875; b) G. Maiti, P. Kundu, C. Guin, *Tetrahedron Lett.* **2003**, *44*, 2757–2758; c) A. S. Paraskar, G. K. Dewkar, A. Sudalai, *Tetrahedron Lett.* **2003**, *44*, 3305–3308; d) N. Fu, Y. Yuan, M. Pang, J. Wang, C. Peppe, *J. Organomet. Chem.* **2003**, *672*, 52–57; e) M. A. P. Martins, M. V. M. Teixeira, W. Cunico, E. Scapin, R. Mayer, C. M. P. Pereira, N. Zanatta, H. G. Bonacorso, C. Peppe, Y. F. Yuan, *Tetrahedron Lett.* **2004**, *45*, 8991–8994; f) G. Jenner, *Tetrahedron Lett.* **2004**, *45*, 6195–6198; g) I. Cepanec, M. Litvic, A. Bartolincic, M. Lovric, *Tetrahedron* **2005**, *61*, 4275–4280; h) H. El Badaoui, F. Bazi, R. Tahir, H. B. Lazrek, S. Sebti, *Catal. Commun.* **2005**, *6*, 455–458; i) S. L. Jain, J. K. Joseph, B. Sain, *Catal. Lett.* **2007**, *115*, 52–55; j) Y. Yu, D. Liu, C. Liu, H. Jiang, G. Luo, *Prep. Biochem. Biotechnol.* **2007**, *37*, 381–387; k) A. Saini, S. Kumar, J. S. Sandhu, *Indian J. Chem.* **2007**, *46B*, 1886–1889; l) H. Khabazzadeh, K. Saidi, H. Sheibani, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 278–280; m) X. Chen, Y. Peng, *Catal. Lett.* **2008**, *122*, 310–313.

[3] a) L. E. Overman, M. H. Rabinowitz, P. A. Renhowe, *J. Am. Chem. Soc.* **1995**, *117*, 2657–2658; b) T. U. Mayer, T. M. Kapoor, S. J. Haggarty, R. W. King, S. L. Schreiber, T. J. Mitchison, *Science* **1999**, *286*, 971–974; c) R. V. Rani, N. Srinivas, M. R. Kishan, S. J. Kulkarni, K. V. Raghavan, *Green Chem.* **2001**, *3*, 305–306; d) I. S. Zorkun, S. Sarac, S. Celebib, K. Erolb, *Bioorg. Med. Chem.* **2006**, *14*, 8582–8589; e) L. M. Ramos, A. Tobio, M. R. dos Santos, H. C. B. de Oliveira, A. F. Gomes, F. C. Gozzo, A. L. de Oliveira, B. A. D. Neto, *J. Org. Chem.* **2012**, *77*, 10184–10193; f) X.-L. Shi, H. Yang, M. Tao, W. Zhang, *RSC Adv.* **2013**, *3*, 3939–3945; g) P. K. Sahu, D. D. Agarwal, *RSC Adv.* **2013**, *3*, 9854–9864.

[4] a) S. Martínez, M. Meseguer, L. Casas, E. Rodríguez, E. Molins, M. M. Mañas, A. Roig, R. M. Sebastián, A. Vallribera, *Tetrahedron* **2003**, *59*, 1553–1556; b) J. Azizian, A. A. Mohammadi, A. R. Karimi, M. R. Mohammadizadeh, *App. Catal. A: Gen.* **2006**, *300*, 85–88; c) S. L. Jain, J. K. Joseph, S. Singhal, B. Sain, *J. Mol. Catal. A: Chem.* **2007**, *268*, 134–138; d) S. L. Jain, V. V. D. N. Prasad, B. Sain, *Catal. Commun.* **2008**, *9*, 499–503; e) P. Li, S. Regati, R. J. Butcher, H. D. Arman, Z. Chen, S. Xiang, B. Chen, C.-G. Zhao, *Tetrahedron Lett.* **2011**, *52*, 6220–6222; f) J. Mondal, T. Sen, A. Bhaumik, *Dalton Trans.* **2012**, *41*, 6173–6181; g) R. K. Sharma, D. Rawat, *Inorg. Chem. Commun.* **2012**, *17*, 58–63; h) R. Tayebee, M. M. Amini, M. Ghadamgahi, M. Armaghan, *J. Mol. Catal. A: Chem.* **2013**, *366*, 266–274; i) F. Zamani, S. M. Hosseini, S. Kianpour, *Solid State Sci.* **2013**, *26*, 139–143; j) G. R. Chaudhary, P. Bansal, S. K. Mehta, *Chem. Eng. J.* **2014**, *243*, 217–224; k) A. Dhakshinamoorthy, H. Garcia, *Chem. Soc. Rev.* **2014**, *43*, 5750–5765.

[5] a) A. P. Wight, M. E. Davis, *Chem. Rev.* **2002**, *102*, 3589–3614; b) A. Stein, *Adv. Mater.* **2003**, *15*, 763–775.

[6] a) D. Y. Zhao, D. J. Goldfard, *J. Chem. Soc. Chem. Commun.* **1995**, 875–876; b) B. J. Aronson, C. F. Blanford, A. Stein, *Chem. Mater.* **1997**, *9*, 2842–2851; c) J. Xu, Z. Luan, M. Hartman, L. Kevan, *Chem. Mater.* **1999**, *11*, 2928–2936; d) M. Fröba, R. Köhn, B. Gaellë, *Chem. Mater.* **1999**, *11*, 2858–2865; e) V. Caps, S. C. Tsang, *Catal. Today* **2000**, *61*, 19–27; f) C. Pak, G. L. Haller, *Microporous Mesoporous Mater.* **2001**, *48*, 165–170; g) R. Radhakrishnan, T. S. Oyama, J. G. Chen, K. Asakura, *J. Phys. Chem. B* **2001**, *105*, 4245–4253; h) E. P. Reddy, *J. Phys. Chem. B* **2002**, *106*, 3394–3401; i) N. Lang, P. Delichere, A. Tuel, *Microporous Mesoporous Mater.* **2002**, *56*, 203–217; j) K. Dhara, K. Sarkar, D. Srimani, S. K. Saha, P. Chattopadhyay, A. Bhaumik, *Dalton Trans.* **2010**, *39*, 6395–6402; k) U. Díaz, D. Brunel, A. Corma, *Chem. Soc. Rev.* **2013**, *42*, 4083–4097.

[7] a) B. Hatton, K. Landskron, W. Whitnall, D. Perovic, G. A. Ozin, *Acc. Chem. Res.* **2005**, *38*, 305–312; b) F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem. Int. Ed.* **2006**, *45*, 3216–3251; *Angew. Chem.* **2006**, *118*, 3290–3328; c) S. Fujita, S. Inagaki, *Chem. Mater.* **2008**, *20*, 891–908; d) Q. Yang, J. Liu, L. Zhang, C. Li, *J. Mater. Chem.* **2009**, *19*, 1945–1955; e) S. El Hankari, B. Motos-Pérez, P. Hesemann, A. Bouhaouss, J. J. E. Moreau, *Chem. Commun.* **2011**, *47*, 6704–6706; f) F. Hoffmann, M. Fröba, *Chem. Soc. Rev.* **2011**, *40*, 608–620.

[8] M. Waki, N. Mizoshita, T. Tani, S. Inagaki, *Angew. Chem. Int. Ed.* **2011**, *50*, 11667–11671; *Angew. Chem.* **2011**, *123*, 11871–11875.

[9] a) C. Baleizão, B. Gigante, D. Das, M. Álvaro, H. Garcia, A. Corma, *J. Catal.* **2004**, *223*, 106–113; b) M. Nandi, P. Roy, H. Uyama, A. Bhaumik, *Dalton Trans.* **2011**, *40*, 12510–12518; c) S. Verma, M. Nandi, A. Modak, S. L. Jain, A. Bhaumik, *Adv. Synth. Catal.* **2011**, *353*, 1897–1902; d) A. Modak, J. Mondal, A. Bhaumik, *Green Chem.* **2012**, *14*, 2840–2855.

[10] a) B. Karimi, D. Elhamifar, J. H. Clark, A. J. Hunt, *Chem. Eur. J.* **2010**, *16*, 8047–8053; b) B. Karimi, D. Elhamifar, J. H. Clark, A. J. Hunt, *Org. Biomol. Chem.* **2011**, *9*, 7420–7426; c) B. Karimi, D. Elhamifar, O. Yari, M. Khorasani, H. Vali, J. H. Clark, A. J. Hunt, *Chem. Eur. J.* **2012**, *18*, 13520–13530; d) D. Elhamifar, B. Karimi, J. Rastegar, M. H. Banakar, *ChemCatChem* **2013**, *5*, 2418–2424; e) B. Karimi, M. Gholinejad, M. Khorasani, *Chem. Commun.* **2012**, *48*, 8961–8963; f) D. Elhamifar, A. Shábani, *Chem. Eur. J.* **2014**, *20*, 3212–3217; g) B. Karimi, F. Bakhshandeh Rostami, M. Khorasani, D. Elhamifar, H. Vali, *Tetrahedron* **2014**, *70*, 6114–6119; h) D. Elhamifar, F. Hosseinpoor, B. Karimi, S. Hajati, *Microporous Mesoporous Mater.* **2015**, *204*, 269–275; i) M. Nasr-Esfahani, D. Elhamifar, T. Amadeh, B. Karimi, *RSC Adv.* **2015**, *5*, 13087–13094.

[11] D. Elhamifar, B. Karimi, A. Moradi, J. Rastegar, *ChemPlusChem* **2014**, *79*, 1147–1152.

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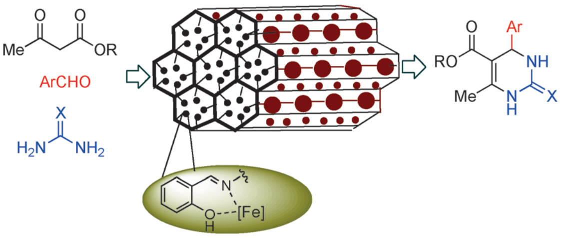
Preparation of Iron-Containing Schiff Base and Ionic Liquid Based Bifunctional Periodic Mesoporous Organosilica and Its Application in the Synthesis of 3,4-Dihydropyrimidinones



Hard graft: A novel iron-containing Schiff base and ionic liquid based bifunctional periodic mesoporous organosilica (Fe@SBIL-BPMO) was prepared and characterized, and its catalytic application was investigated in the one-pot three-component Biginelli reaction (see picture). The catalyst illustrated excellent reactivity, recoverability, and reusability under the applied conditions.