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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Perlite: A cheap and natural support for heterogenization of HBF_4

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

5 Nano-Perlite-fluoroboric acid (n-PeFBA) has been synthesized by immobilization of HBF_4 on perlite as naturally and cheap support to produce an efficient green heterogeneous reusable solid acid catalyst. The synthesized n-PeFBA was fully characterized by spectroscopic techniques (FE-SEM, EDX, BET and BJH). The catalyst exhibited excellent activity for the synthesis of biologically important 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles in high to excellent yields and selectivities. This
10 newly synthesized heterogeneous solid acid catalyst has advantages such as low cost, ease of handling, ease of preparation, high stability and reusability and low toxicity. Our study showed that the catalyst could be recovered and reused for several runs without noticeable deterioration in catalytic activity.

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1. Introduction

In the current chemical industries, novel catalytic technology has formed the foundation of the process novelty, and at least one catalytic process has been used in the production of 90% of the existing chemicals.¹ Evolution of clean and environmentally benign chemical processes using less hazardous catalysts has become a primary goal in synthetic organic chemistry. To date, liquid acids are the most widely used as catalysts for organic transformations.²⁻⁴ However, the traditional homogeneous catalytic systems suffer from drawbacks in terms of difficulties in separating, recycling and the generation of large amounts of waste. Therefore, utilization of these catalysts can result in unacceptably high manufacturing costs.^{5, 6} To overcome the aforementioned problems, replacement of environmental hazardous Bronsted and Lewis acid catalysts with efficient reusable solid acid catalysts have received considerable attention because of their unique properties such as high reactivity, operational simplicity and non-corrosive nature. In particular, running a reaction under heterogeneous condition is more promising since it involves the facile recovery and reuse of the catalyst.⁷⁻¹⁷ Therefore, heterogeneous solid acid catalysts can play a significant role in the development of Green Chemistry.

Perlite is a cheap mineral mixed oxide mixture which contains approximately 70-75% of SiO₂ and 12-18% of Al₂O₃¹⁸ that can be used as a platform for the preparation of the above mentioned catalyst, because it has many advantages such as ease of handling, low cost, low toxicity, high mechanical and thermal stability and non-corrosiveness.¹⁹⁻²²

Imidazole and their derivatives have been identified as important classes of heterocycles due to their wide range of biological and therapeutic properties such as anti-inflammatory agents,²³ anti-bacterial agents,²⁴ glucagon receptor antagonists,²⁵ modulators of Pgp-mediated multidrug resistance,²⁶ ligands of the Src SH2 protein,²⁷ antitumor agents,²⁸ and CB1 cannabinoid receptor antagonists,²⁹ as well as in photography as light-sensitive materials. They are also known as inhibitors, fungicides and herbicides,³⁰ plant growth regulators and therapeutic agents.³¹ Thus, the syntheses of imidazole derivatives are currently of great interest. Numerous classical methods for the synthesis of multisubstituted imidazoles have been reported. Common synthetic method for the synthesis of 2,4,5-trisubstituted imidazoles is the multicomponent reaction approach involving the cyclocondensation of a 1,2-diketone, α -hydroxy/acetoxysilyloxyketone or 1,2-ketomonoxime, aldehyde and ammonium acetate, which comprise the use of refluxing in acetic acid,³² in the presence of a homogeneous strong protic acid,³³ Lewis acids,³⁴⁻³⁶ glycerol,³⁷ ionic liquids^{38, 39} and under microwave/ultrasonic/classical heating in the presence or absence of catalyst.⁴⁰⁻⁴² On the other hand, The 1,2,4,5-trisubstituted imidazoles are generally synthesized by the reaction of a 1,2-diketone, α -hydroxy/acetoxysilyloxyketone or 1,2-ketomonoxime, aldehyde, amine and ammonium acetate using microwaves,⁴³ ionic liquids,⁴⁴ BF₃·SiO₂,⁴⁵ L-Proline,⁴⁶ HClO₄-SiO₂,⁴⁷ heteropolyacid,⁴⁸ Sodium Benzenesulfinate⁴⁹ and molecular iodine.⁵⁰ Some of these synthetic methods suffer from one or more drawbacks, such as stringent conditions, long reaction times, unsatisfactory yields, difficult work-up procedures, expensive reagents, difficulty in

recovery and reusability of the catalysts and no agreement with the green chemistry protocols. Therefore there is a need for development of simple and efficient catalyst for the preparation of 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles.

Recently, we prepared perlite sulfonic acid and investigated its application as an efficient catalyst in several organic reactions.⁵¹ Our study illustrated that this catalyst had excellent reactivity in multicomponent one-pot synthesis of heterocyclic compound such as 3,4-dihydropyrimidin-2(1H)-ones, 2,4,5-trisubstituted imidazoles, coumarins and bis(indolyl)methanes. Moreover, the catalyst was successfully recovered and reused several times without significant decrease in activity.

In spite of the remarkable properties of perlite and the importance of heterogeneous solid acid catalysts in the chemistry world, according to our research, there is no report on the preparation of fluoroboric acid adsorbed on perlite in the literature.

In continuation of these studies, here in we have prepared and characterized a novel nano-Perlite-fluoroboric acid (n-PeFBA) and studied its catalytic performance in the one-pot synthesis of 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles. Moreover, the reactivity, reusability, and stability of the catalyst during reactions have also been investigated in detail.

2. Result and Discussion

As a part of our ongoing investigation in developing new and efficient heterogeneous solid acid catalysts,^{8, 51} we demonstrate here the synthesis of nano-Perlite-fluoroboric acid (n-PeFBA) and discuss its performance as solid acid catalyst. The n-PeFBA was prepared by the reaction of perlite and fluoroboric acid at room temperature. The "inorganic solid acid catalysts" were characterized *via* EDX, FE-SEM and BET and BJH analysis.

2.1. Characterization of n-PeFBA

2.1.1. XRD Energy-dispersive X-ray spectroscopy (EDX) analysis

Energy-dispersive X-ray spectroscopy (EDX) analysis of n-PeFBA indicated the presence of Si, Al, Fe, K, Na, Mg, O as the components of perlite structure, also the small peaks for fluorine and boron clearly indicate that HBF₄ is incorporated within the channels of Perlite (Fig. 1).

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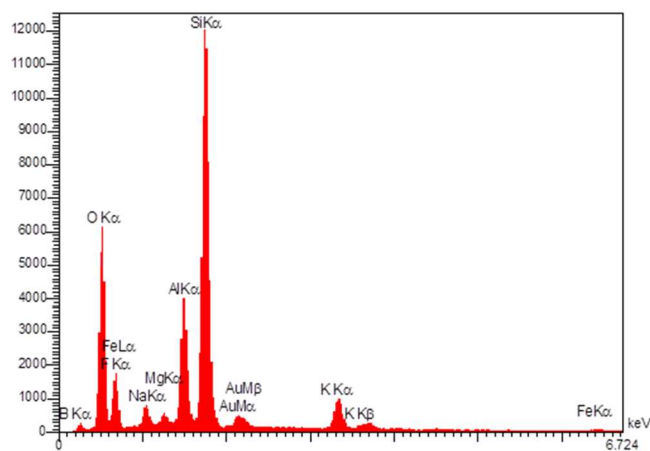


Fig. 1. EDX spectra of n-PeFBA

2.1.2. SEM Analysis of the catalyst

Fig. 2 shows the field emission scanning electron microscopy (FE-SEM) images of perlite and modified perlite nanostructures. Figs. 2a and b show that the pure perlite has a layer structure with smoothed surface. Figs. 2c and d show the morphology of n-PeFBA upon functionalization. It is clear that the morphology of the n-PeFBA is a layer like structure but it is not smooth. The size and morphology distribution of the particles located on the layer are homogeneous. The layer thickness size is about 50-70 nm and the particles diameter sizes are about 50-70 nm. It shows that the modification process has been performed successfully.

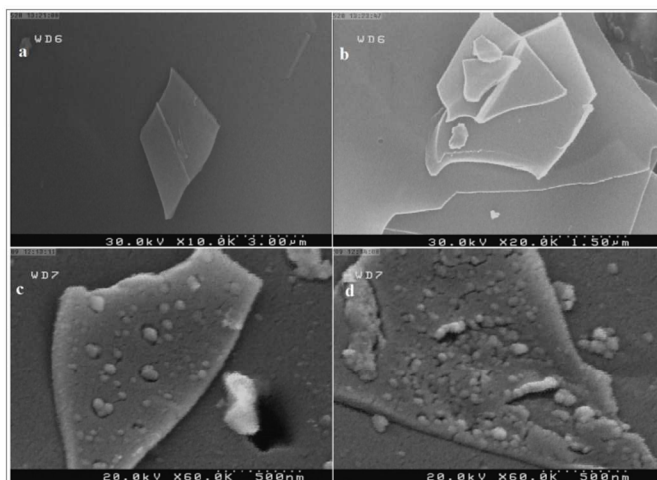


Fig. 2. FE-SEM images of perlite (a,b) and n-PeFBA (c,d)

2.1.3. BET and BJH texture analysis of the catalyst

The synthesized powders were characterized for their surface area,

average pore size and average pore volume. Prior to N₂-physical adsorption measurement, the samples were degassed at 150 °C for 120 min in the nitrogen atmosphere. So, the specific surface area (SBET) of the obtained materials was determined with adsorption-desorption isotherms of N₂ at 77 K. The surface area, pore volume and average pore diameter of the synthesized materials are summarized in table 1. From table 1, it can be seen that the average surface area and pore volumes are about 0.21 m² g⁻¹ and 0.0003 cm³ g⁻¹ for pure perlite and 0.43 m² g⁻¹ and 0.0043 cm³ g⁻¹ for modified perlite, respectively. And also, for perlite and n-PeFBA, the average nanoparticles sizes were measured as 29 μm and 14 μm, respectively. Also, table 2 shows the textural properties of the as-prepared materials. The data summarized in table 2 shows that the specific surface area of pores of n-PeFBA is larger than that of pure perlite and the pore width and pore volume of n-PeFBA is larger than that of perlite. So, the investigated results of BET and BJH measurements suggest that the surface area of modified perlite is larger than that of pure perlite. It also shows that with modifying perlite, the average particle sizes are smaller than those of pure perlite that is in a good agreement with FESEM images.

Table 1. Pore structure parameters of perlite and n-PeFBA derived from the N₂ adsorption-desorption isotherms.

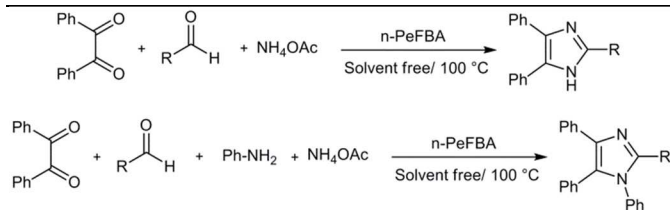
Sample	BET surface area (m ² g ⁻¹)	Pore size (Å)	Pore volume (cm ³ g ⁻¹)	Average particles size (μm)
perlite	0.21	64	0.0003	29
n-PeFBA	0.42	408	0.0043	14

Table 2. BJH data (textural properties) for the perlite and n-PeFBA

Property	perlite	n-PeFBA
BJH adsorption cumulative surface area of pores between 17 and 3000Å width	0.09 m ² g ⁻¹	0.41 m ² g ⁻¹
BJH adsorption cumulative volume of pores between 17 and 3000Å width	0.0007 cm ³ g ⁻¹	0.0052 cm ³ g ⁻¹
BJH adsorption average pore width (4V/A)	64 nm	41 nm

2.2. Application of n-PeFBA as heterogeneous catalyst in the synthesis of multisubstituted imidazoles

We wish to report that immobilization of fluoroboric acid on perlite (n-PeFBA) catalyzed the synthesis of 2,4,5-trisubstituted imidazoles from aromatic aldehydes, benzil and NH₄OAc and the synthesis of 1,2,4,5-tetrasubstituted imidazoles from aromatic aldehydes, benzil, NH₄OAc and aniline was also described. In pursuit of developing a solvent-free methodology for the preparation of these biologically important compounds, we decided to explore the use of this nanocatalyst for the synthesis of various multisubstituted imidazoles under solvent-free condition (Scheme 1).



Scheme 1. Synthesis of 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted using of n-PeFBA

2.2.1. Optimization of the reaction parameters

In a model study, to achieve suitable conditions for the synthesis of 2,4,5-trisubstituted imidazoles, the reaction of benzaldehyde (1 mmol), benzil (1 mmol), and ammonium acetate (2 mmol) was carried out in the presence of various amount of the n-PeFBA and the results are presented in Table 3, entries 1–4. Maximum yield was obtained with 0.01 mmol of catalyst (Table 3, entry 2). The usage of higher amounts of catalyst did not have any significant effect on the product yield. Also, when the reaction was attempted without the addition of catalyst, no desired product was obtained (Table 3, entry 1). The effect of temperature plays an important role in the catalytic synthesis of imidazoles. It was examined in the temperature range from 60 °C to 120 °C in the absence of solvent, using n-PeFBA as catalyst. At 60 °C the reaction has not high yield and with further increase in temperature to 100 °C the yield of product increased. By increasing the temperature to 120 °C, the yield of product decreased which may be due to the formation of some side product (Table 3, entries 2, 5-7). So 100 °C was chosen as the optimum temperature for performing the reaction. We also examined the effect of different solvents such as H₂O, MeOH and CH₃CN on a model reaction (Table 3, entries 8-10). Among the solvents examined, H₂O and MeOH are suitable reaction media (Table 3, entries 8, 10), whereas in CH₃CN did not afford any desired product (Table 3, entry 9). The

reaction proceeded under solvent-free condition to generate the corresponding product in excellent yields in short reaction time in comparison with solvent conditions (Table 3, entry 2). So, to avoid the use of volatile solvent and to reduce environmental pollution, all the reactions were performed under solvent-free conditions.

Table 2. Optimization of synthesis of imidazoles^a

Entry	Solvent	Condition	Amount of Catalyst (mmol)	Time (min)	Yield (%)
1	Solvent-free	100 °C	-	35	trace
2	Solvent-free	100 °C	0.01	35	98
3	Solvent-free	100 °C	0.02	35	84
4	Solvent-free	100 °C	0.025	35	82
5	Solvent-free	60 °C	0.01	35	70
6	Solvent-free	80 °C	0.01	35	79
7	Solvent-free	120 °C	0.01	35	90
8	H ₂ O	Reflux	0.01	35	70
9	CH ₃ CN	Reflux	0.01	35	79
10	MeOH	Reflux	0.01	35	90

^a Reaction condition: benzaldehyde (1 mmol), benzil (1 mmol), NH₄OAc (2 mmol).

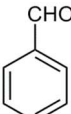
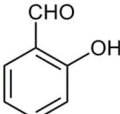
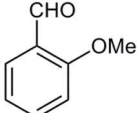
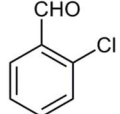
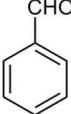
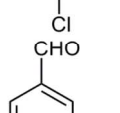
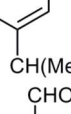
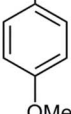
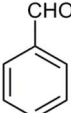
In order to study the generality of the procedure, this process was demonstrated by several substituted aromatic aldehydes to synthesize the corresponding 2,4,5-trisubstituted imidazoles under the optimized conditions in good yields (Table 4). Aldehydes bearing either electron-withdrawing or electron-donating groups perform equally well in the reaction and all products were obtained in high yields. The nature of the substituents on the aromatic aldehyde has not significant effect on yield of reaction. However the nature of catalyst is significant. The present reaction conditions were also effective in the synthesis of 1,2,4,5-tetrasubstituted imidazoles. The results of synthesis of 1,2,4,5-tetrasubstituted imidazoles from benzil, aniline, ammonium acetate and various aromatic aldehydes tabulated in Table 5.

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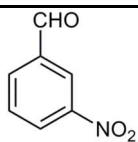
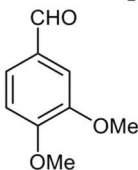
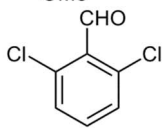
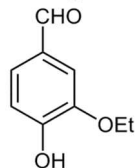
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Table 3. n-PeFBA-catalyzed one-pot synthesis of 2,4,5-trisubstituted imidazoles^a

Entry	Aldehydes	Time (min)	Yield (%)	mp (°C)	
				Found	Reported (ref.)
1		35	98	267-268	267-269 ³⁷
2		60	88	211-213	204-205 ³⁷
3		45	89	208-210	210 ⁵²
4		40	87	196-198	195-197 ⁵³
5		48	97	264-266	264-267 ⁵⁴
6		41	93	253-255	252-255 ⁵⁵
7		35	96	220-222	220-222 ³⁷
8		34	94	233-235	232-234 ⁵⁶
9		65	75	257-258	256-258 ⁵⁷

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10		120	70	320-322	319-321 ³⁷
11		30	92	220-222	222-224 ⁵⁷
12		48	89	236-238	228-231 ⁵⁷
13		80	94	264-266	268-269 ³⁷

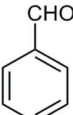
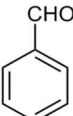
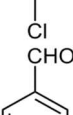
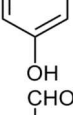
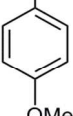
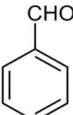
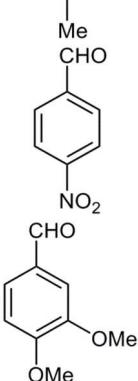
^a Reaction condition aromatic aldehyde (1 mmol), benzil (1 mmol), NH₄OAc (2 mmol), n-PeFBA (0.01mmol), solvent-free, 100 °C.

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Table 4. n-PeFBA-catalyzed one-pot synthesis of 1,2,4,5-tetrasubstituted imidazoles^a

Entry	Aldehydes	Time (min)	Yield (%)	mp (°C)	
				Found	Reported
1		80	92	218-219	218-219 ³⁷
2		120	91	185-187	164-166 ⁵⁸
3		90	89	283-285	282-284 ⁵⁶
4		120	90	180-183	180-182 ⁵⁶
5		120	97	184-186	182-184 ⁵⁶
6		180	78	220-222	184-186 ⁵⁶
7		110	93	178-180	178-180 ⁵⁹

^a Reaction condition aromatic aldehyde (1 mmol), benzil (1 mmol), NH₄OAc (1 mmol), aniline (1 mmol), (0.01mmol), solvent-free, 100 °C.

A comparison among n-PeFBA and the other catalysts, which were reported in the literature, in synthesis of 2,4,5-trisubstituted imidazoles and 1,2,4,5-tetrasubstituted imidazoles revealed

advantages of this nanocatalyst over the most of them in term of reaction conditions, time and product yield (Table 6 and 7).

Table 5. Comparison of the efficiency of various catalysts with n-PeFBA in the synthesis of 2,4,5-trisubstituted imidazoles.

Entry	Catalyst	Condition	Time (min)	Yield (%)	Ref.
1	Yb(OPf) ₃	C ₁₀ F ₁₈ /80 °C	360	80	⁶⁰
2	Nano-crystalline SZ ^a	Reflux in EtOH	45	87	⁵⁶
3	NiCl ₂ ·6H ₂ O/Al ₂ O ₃	Reflux in EtOH	90	89	³⁵
4	Zeolite	Reflux in EtOH	60	80	⁵⁶
5	Montmorillonite K10	Reflux in EtOH	90	75	⁵⁶
6	n-PeFBA	Solvent free/ 100 °C	35	98	Present work

^a sulfated zirconia**Table 6.** Comparison of the efficiency of various catalysts with n-PeFBA in the synthesis of 1,2,4,5-tetrasubstituted imidazoles.

Entry	Catalyst	Condition	Time (min)	Yield (%)	Ref.
1	BF ₃ /SiO ₂	Solvent free/ 140 °C	120	92	⁶¹
2	NaHSO ₄ /SiO ₂	Solvent free/ 140 °C	120	92	⁶²
3	SbCl ₅ /SiO ₂	Solvent free/ 140 °C	120	90	⁶³
4	MgCl ₂	Solvent free/ 80 °C	45	60	⁴⁵
5	n-PeFBA	Solvent free/ 100 °C	80	92	Present work

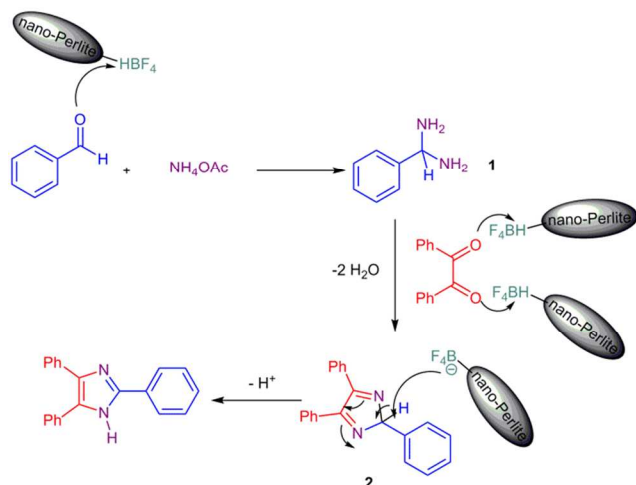
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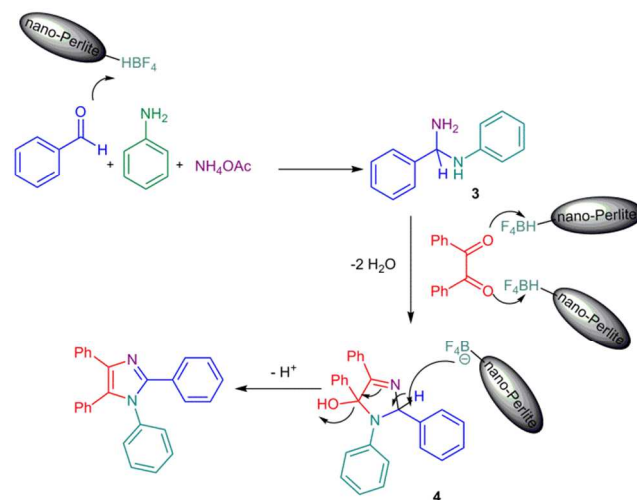
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2.3. Plausible mechanism

Considering the general mechanistic pathway, the suggested mechanism for the formation of trisubstituted imidazole using n-PeFBA is depicted in Scheme 2. The reaction was initiated through protonation by n-Perlite-HBF₄ at one of its carbonyl oxygens for the formation of diamine intermediate **1**. The electrophilicity of the carbonyl group of the aldehyde was thereby increased. Intermediate **1**, condenses with benzil to form intermediate **2**, which in turn rearranges to the trisubstituted imidazole (Scheme 2). Similarly, the plausible mechanism for the synthesis of the tetrasubstituted imidazole involves the formation of intermediate **3** by the reaction of an aldehyde, phenyl amine and ammonium acetate in the presence of catalyst. Intermediate **3** condenses with benzil to form intermediate **4**, and then the tetrasubstituted imidazole (Scheme 3).



Scheme 2. Proposed mechanism for the synthesis of trisubstituted imidazole



Scheme 3. Proposed mechanism for the synthesis of tetrasubstituted imidazole

2.4. Reusability of the catalyst

The activity of the recycle catalyst was also examined under the optimized conditions. Upon completion, the heterogeneous catalyst was separated using centrifuge and was washed with acetone/ethanol, dried in oven and the recycled catalyst was saved for the next reaction. The recycled catalyst could be reused 5 runs without distinct deterioration in catalytic activity (Fig. 3).

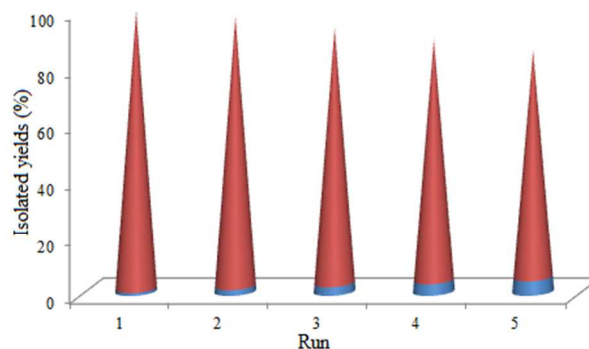


Fig. 3. Recyclability of n-PeFBA

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3. Experimental section

3.1. General Remarks

All of the chemicals used in this study were purchased from Merck and Aldrich chemical companies and used without further purification. Perlite obtained from Iran, Semnan sources. All yields refer to the isolated products after purification. Products were characterized by their physical constants and comparison

with authentic samples. The purity of products was accompanied by thin layer chromatography (TLC) on silica-gel polygram SILG-UV 254 plates using n-hexane/ethyl acetate mixture as mobile phase. Melting points were determined on Electro thermal 9100 without further corrections. The EDX characterization of the catalyst was performed using a Mira 3-XMU scanning electron microscope equipped with an energy dispersive X-ray spectrometer operating. Filed emission scanning electron microscope (FESEM) images were obtained on a SEM-Philips XL30. BET surface areas were acquired on a Beckman Coulter SA3100 surface area analyzer. The NMR spectra were measured in pure deuteriated chloroform and dimethyl sulfoxide with a Bruker Avance 300 MHz instruments (^1H NMR 300 MHz) with tetramethylsilane (TMS) as the internal reference.

3.2. Providing of neat perlite powder

10 g of perlite powder was washed by stirring overnight in 200 ml methanol and ethanol to remove organic components, then were washed by distilled water, methanol and ethanol three times and following that were heated in aqueous solution of NaOH 5N for 20 minutes. Precipitated perlite were filtered and rinsed with excess water until NaOH removed and then dried at $100\text{ }^\circ\text{C}$.⁵¹

3.3. Preparation of fluoroboric acid adsorbed on perlite (n-PeFBA)

The n-PeFBA was prepared following the originally reported procedure for the preparation of $\text{HBF}_4\text{-SiO}_2$.⁶⁴ A magnetically stirred suspension of perlite (26.7 g) in Et_2O (75 mL) was treated with HBF_4 (3.3 g, 15 mmol, 8.25 mL of a 40% aq solution of HBF_4) and the mixture was stirred magnetically for 3h at room temperature. The mixture was concentrated and the residue dried under vacuum at $100\text{ }^\circ\text{C}$ for 72 h to afford n-PeFBA (0.5 mmol of $\text{HBF}_4\text{ g}^{-1}$) as a free-flowing powder.

3.4. n-PeFBA, solid acid catalyst for multi component one-pot synthesis of imidazoles

3.4.1. General procedure for the synthesis of 2,4,5-trisubstituted imidazoles

The stirred mixture of aldehyde (1 mmol), benzil (1 mmol) and NH_4OAc (2 mmol) was heated at $100\text{ }^\circ\text{C}$ (bath temperature) in the presence of n-PeFBA (0.01 mmol) under neat conditions for the appropriate time until the reaction was complete. The reaction was monitored by thin layer chromatography (TLC) [7:3 hexane:ethyl acetate].

After the completion of the reaction, hot ethanol (5 mL) was added and the obtained solution was hotly filtered. The filtrate was then sufficiently cooled to precipitate crude products. The retaining catalyst was washed with EtOH (2×4 mL). The combined filtrates were concentrated under rotary vacuum evaporation and the crude product recrystallized from ethanol to afford pure imidazole derivatives. The products were confirmed by comparisons with authentic samples, IR, ^1H NMR spectra and melting points.

3.4.2. General procedure for the synthesis of 1,2,4,5-tetrasubstituted imidazoles

The mixture of aldehyde (1 mmol), benzil (1 mmol), NH_4OAc (1 mmol) and aniline (1 mmol) was heated at $100\text{ }^\circ\text{C}$ (bath temperature) in the presence of n-PeFBA (0.01 mmol) under solvent free conditions for the appropriate time. After the completion of the reaction which was monitored by TLC, the reaction mixture was diluted with hot ethanol (5 mL) and the obtained solution was hotly filtered. The filtrate was then sufficiently cooled to precipitate crude products. The retaining

catalyst was washed with EtOH (2×4 mL). The combined filtrates were concentrated under rotary vacuum evaporation and the crude product recrystallized from ethanol to afford pure imidazole derivatives. The remaining reactions were performed following this general procedure and the physical data (mp, IR, NMR) of all known compounds were identical with those reported in the literature.

3.5. Selected data

3.5.1. Compound (entry 3, Table 4). 2-(2-Methoxy-phenyl)-4,5-diphenyl-1H-imidazole: m.p. $208\text{--}210\text{ }^\circ\text{C}$, IR (KBr, cm^{-1}). 3400, 1650, 1600, 1475, 1180 ^1H NMR (DMSO-d_6) δ . 3.88 (s, 3H), 6.86-8.02 (m, 14H), 11.85 (s, 1H).

3.5.2. Compound (entry 11, Table 4). 2-(3,4-Dimethoxyphenyl)-4,5-diphenyl-1H-imidazole: m.p. $220\text{--}222\text{ }^\circ\text{C}$, IR (KBr, cm^{-1}). 3400, 3100, 2874, 1650, 1600, 1475, 1255, 1100, 900, 750, 690. ^1H NMR (DMSO-d_6) δ . 3.13 (s, 3H), 3.81(s, 3H), 7.01-7.63 (m, 13H), 12.47 (s, 1H).

3.5.3. Compound (entry 13, Table 4). 2-ethoxy-4-(4,5-Diphenyl-1H-imidazol-2-yl)-phenol: m.p. $264\text{--}266\text{ }^\circ\text{C}$, IR (KBr, cm^{-1}). 3224, 1589, 1473, 1180 ^1H NMR (DMSO-d_6) δ . 1.39 (t, 3H), 4.11 (q, 2H), 6.87 (d, 1H), 7.22-7.55 (m, 11H), 7.63 (d, 1H), 9.23 (s, 1H), 12.43 (s, 1H).

3.5.4. Compound (entry 4, Table 5). 1,4,5-Triphenyl-2-(4-methoxyphenyl)-1H-imidazole: m.p. $180\text{--}183\text{ }^\circ\text{C}$, IR (KBr, cm^{-1}). 3035, 1596, 1396, 1087 ^1H NMR (CDCl_3) δ . 3.81 (s, 3H), 7.50 (d, 2H), 7-7.21 (m, 17 H).

3.5.5. Compound (entry 5, Table 5). 1,4,5-Triphenyl-2-p-tolyl-1H-imidazole: m.p. $184\text{--}186\text{ }^\circ\text{C}$, IR (KBr, cm^{-1}). 3042, 2944, 1667, 1591, 1092 ^1H NMR (CDCl_3) δ . 2.30 (s, 3H), 7.62 (d, 2 H), 7.31-7.02 (m, 17H), 6.98 (d, J=8.8 Hz, 2H).

4. Conclusion

In the present work, the novel nano solid acid catalyst was developed and exhibited highly catalytic activity for the one-pot synthesis of 2,4,5-trisubstituted imidazoles and 1,2,4,5-tetrasubstituted imidazoles under solvent-free conditions. Inexpensive, heterogeneous and non-toxicity nature, low-cost, easy preparation, high surface area, large pore size are significant properties of this catalyst. Moreover, the catalyst was proved to be a recyclable, green, and highly effective nano solid acid catalyst.

Acknowledgement

The authors are grateful to the Semnan University research council for the partial support of this work.

Notes

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