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PAPER

Nano Brönsted solid acid containing double-charged diazoniabi-cyclo[2.2.2]octane chloride supported on nano rice husk silica: An efficient catalyst for the one-pot synthesis of phthalazine compounds

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In the present work, amorphous silica nanoparticles were synthesized from low-cost rice husk ash (RH-SiO₂). The nanoparticles were later modified by acidic ionic liquid containing double-charged diazoniabi-cyclo[2.2.2]octane chloride using sol-gel method (RH@[SiPrDABCO@BuSO₃H]HSO₄). The structural properties of this Brönsted solid acid was systematically investigated by fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), thermal gravimetric analysis - derivative thermogravimetric analysis (TGA-DTG), and Brunauer Emmett Teller (BET). The catalytic activity of this nanocomposite was successfully tested in through one-pot synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones via three-component couplings of phthalhydrazide, aromatic aldehydes, and malononitrile. The heterogeneous catalyst could be recovered easily and reused without significant loss of its catalytic activity.

1. Introduction

In recent years, regarding the green chemistry's goals, the target of science and technology has been shifting towards more environment friendly, sustainable resources and reusable catalysts.^{1,2} Because of high surface area, stability, easy synthesis and easily separation, thus for facilitating easy catalyst recycling, silica has been used as heterogeneous catalytic support.³

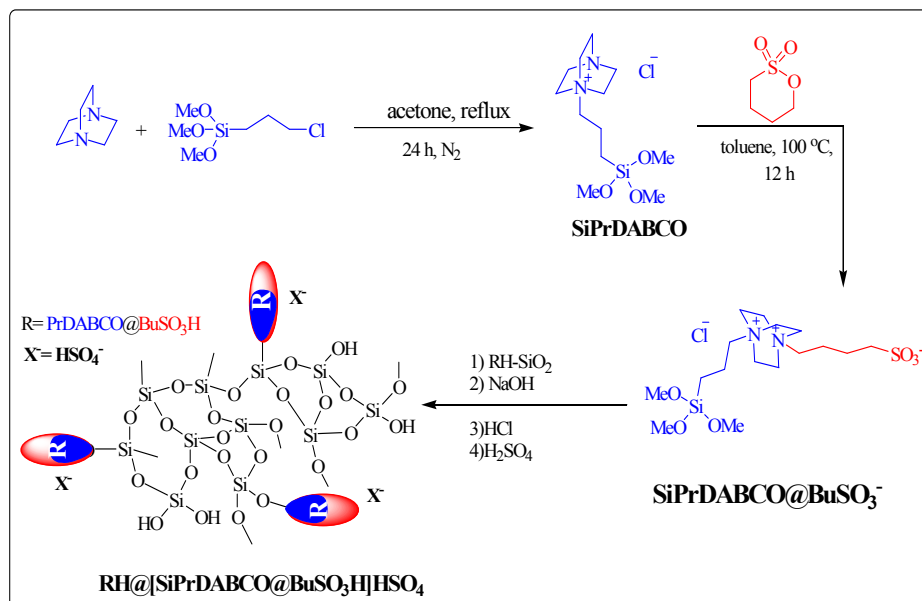
Silica is the major inorganic constituent of the rice husk which high-surface area amorphous silica is extracted by carrying out an acid chemical treatment followed by the process of burning. Preparation of silica from rice husk offers a smart and cheap alternative to commercial silica and at the same time helps solve rice husk disposal problem faced by rice milling industry. In most rice producing countries, rice husk will normally be burnt away causing environmental and health problems. Recently, various types of transition metals were incorporated into rice husk silica and their catalytic potentials in the oxidation, reduction, acylation and benzylation reactions were studied.⁴⁻⁷

Moreover the application of supported ionic liquid (IL) in catalysis is a trendy frontier of researches in recent years. Both in the washing of the homogeneous IL catalyst system for reuse and the separation of product from the ionic liquid, large amounts of organic solvents were usually used. Therefore, supporting ionic liquids on solid is one of the important routes for developing

novel heterogeneous catalysts.⁸ The resulting material is solid and the ionic species is dissolved in both water and organic solvent which can act as a suitable catalyst.^{9,10} Herein, acidic ionic liquids including the Lewis and the Brönsted ones had proved to be efficient catalysts in organic transformation.¹¹ In this regard, there has been considerable interest in the development of stable and recycle solid acids containing ionic liquid part as eco favorable replacements for their homogeneous analogous.¹²

Hybrid organic-inorganic sulfonic acid catalysts offer an alternative support to silica-based materials. Herein, covalently grafting n-propyl and n-butyl sulfonic acids to the supports for generate strong acid sites, has been applied as effective solid acid catalysts in organic transformations. In these types of solid acid catalysts, the reactive centers are highly mobile similar to that of homogeneous catalysts. Synthesis of these materials was conducted by oxidation of immobilized thiols to sulfonic acids or ring opening reaction of 1,3 and 1,4-propanesultone. In both cases, sulfonic acid groups are introduced on the surface via covalently bonds. However, in SH oxidation method, imperfect oxidation of SH groups decreases the efficiency of the catalyst.¹³⁻¹⁵

In the past few decades, heterocyclic chemistry has been one of the most important disciplines in organic synthesis and pharmaceutical chemistry.¹⁶ Heterocyclic compounds containing



Scheme 1 The reaction sequence for the preparation of $\text{RH@[SiPrDABCO@BuSO}_3\text{H]HSO}_4$

phthalazine moiety have received considerable attention because of their pharmacological and biological activities.¹⁷⁻¹⁹ Similarly, heterocycles containing pyrazoles moiety are of current interest due to their wide range of interesting properties, such as anti-hyperglycemic, analgesic, anti-inflammatory, anti-pyretic, anti-bacterial, and anti-viral activities.²⁰⁻²⁶

Several methods for the synthesis of heterocycles containing a phthalazine ring fragment have also been reported. However, each of the known procedures has its merits, but the generality of the existing reports is somewhat defected by the vigorous reaction conditions, and the catalysts and solvents used are not acceptable in the context of green synthesis. Thus further studies and development of simple and highly efficient methodologies are still necessary to overcome these drawbacks.

The aim of this protocol is to highlight the synergistic effects of the combined use of multicomponent coupling reactions and application of solid Brönsted acid catalyst containing ionic liquid part which supported on nanostructure materials for the development of new eco-compatible strategy for the synthesis of heterocycles containing a phthalazine ring fragment.

2. Results and discussion

Investigation around the approach of $\text{RH@[SiPrDABCO@BuSO}_3\text{H]HSO}_4$ preparation and its structural and morphological analysis

There were few studies about the preparation of silica-supported acidic ionic liquid catalyst and its application for multi-component reactions (MCRs). However, as a part of our ongoing interest in the synthesis of biologically relevant heterocyclic compounds,²⁷⁻³⁰ we attempted to design an inorganic-organic hybrid solid Brönsted acid catalyst containing double-charged diazoniabi-cyclo[2.2.2]octane chloride supported on rice husk silica, $\text{RH@[SiPrDABCO@BuSO}_3\text{H]HSO}_4$, for efficient and convenient synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione. Scheme 1 shows the schematic representation of the

synthetic pathway for $\text{RH@[SiPrDABCO@BuSO}_3\text{H]HSO}_4$ solid acid catalyst.

Amorphous nano silica was easily extracted from rice husk (RH). A brief description of the extraction process follows (Fig. 1).

Pretreatment step: to reduce metallic impurities of RH to negligible levels, the clean RH was treated with nitric acid.

Pyrolysis step: to complete combustion, the acid-leached RH was burned in a furnace at 800 °C.

Digestion step: to digestion of the rice husk ash (RHA), the white RHA was reacted with caustic at specific conditions. In this process the silica in the ash was dissolved with caustic soda to form sodium silicate solution.

Precipitation step: the sodium silicate solution was titrated with nitric acid until the solution pH reached to 5.0. in order to precipitate silica.

The FT-IR spectra of $\text{RH@[SiPrDABCO@BuSO}_3\text{H]HSO}_4$, RH-SiO_2 , SiPrDABCO and $\text{SiPrDABCO@BuSO}_3\text{H}$ are shown in Fig. 2. In all materials, the typical bands around 990-1220, 801 and 473 cm^{-1} were attributed to the presence of Si-O group. The band around 1635 cm^{-1} is also due to the bending vibration of water molecules bound to the silica matrix. The presence of peaks at 1200-1500 and 2870-3040 cm^{-1} in the $\text{RH@[SiPrDABCO@BuSO}_3\text{H]HSO}_4$, SiPrDABCO and $\text{SiPrDABCO@BuSO}_3\text{H}$ were most probably due to the C-H bonds and also a band around 1465 cm^{-1} is characteristic for the tertiary amine group.

Scanning electron microscopy (SEM) is a useful tool for determining the size distribution, particle shape and porosity. It has been a primary tool for characterizing the surface morphology and fundamental physical properties of the surface. The morphological features and the particle size distribution of extracted nano silica and $\text{RH@[SiPrDABCO@BuSO}_3\text{H]HSO}_4$ were performed by measuring SEM.

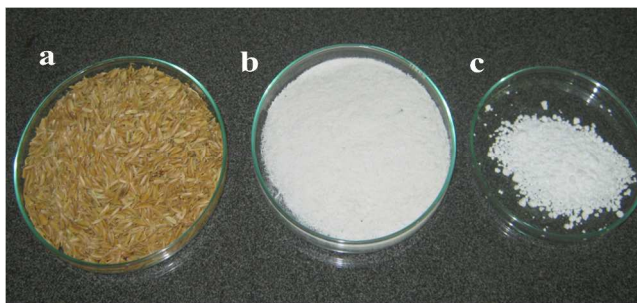


Fig. 1 Macroscopies of RH: (a) as received; (b) after pretreatment and pyrolysis steps; (c) after digestion and precipitation steps

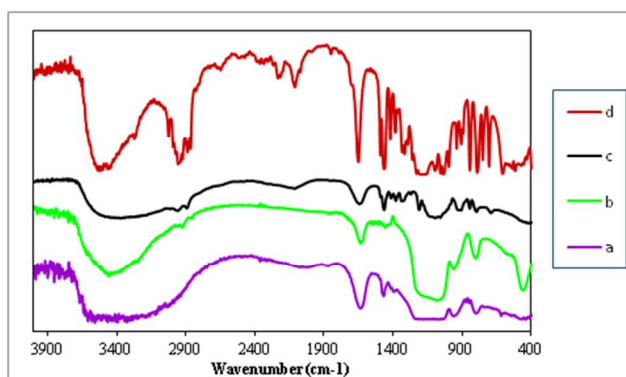


Fig. 2 The FT-IR spectra of (a) RH@[SiPrDABCO@BuSO₃H]HSO₄, (b) RH-SiO₂, (c) SiPrDABCO and (d) SiPrDABCO@BuSO₃H

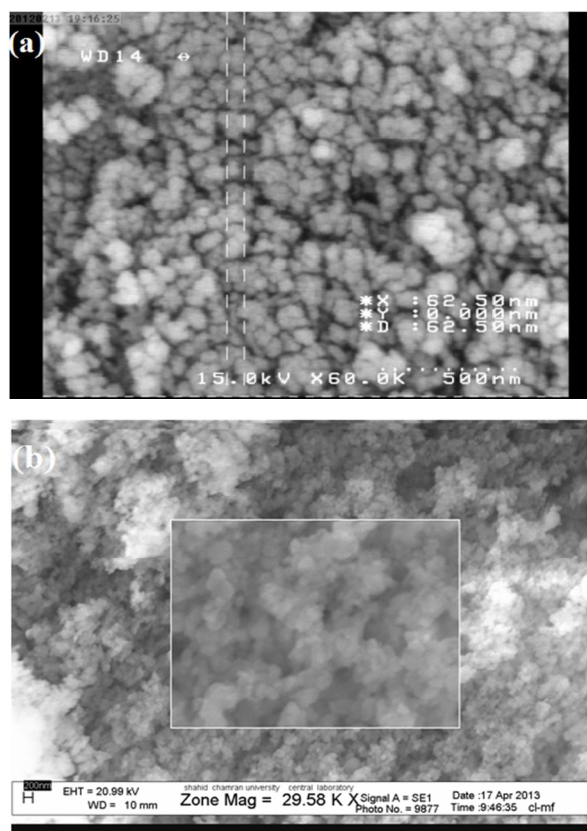


Fig. 3 SEM images of (a) RH-SiO₂ and (b) RH@[SiPrDABCO@BuSO₃H]HSO₄

10 According to Fig. 3, extracted nano silica has spherical shape with nano dimension ranging from 60 to 90 nm and the size of the RH@[SiPrDABCO@BuSO₃H]HSO₄ microspheres are around 150-170 nm, which indicate that the organic-inorganic hybrid silica is successfully anchoring to the magnetic particles.

15 The thermal stability of nanocomposite was also investigated by thermal gravimetric analysis-derivative thermogravimetric analysis (TGA-DTG). TGA-DTG thermogram of RH@[SiPrDABCO@BuSO₃H]HSO₄ in N₂ atmosphere was shown the mass loss of the organic materials as they decompose

20 upon heating (Fig. 4). The 12.8 % weight loss below 150 °C might be due to the loss of the adsorbed water molecules adsorbed onto the surface and ionic liquid part. The weight loss of about 40 % between 150 and 660 °C may be associated to the thermal decomposition of PrDABCO@BuSO₃H. On the basis of

25 this observation, the well grafting of SiPrDABCO@BuSO₃H on the RH-SiO₂ was also verified. In the field of solid catalysis, N₂ adsorption-desorption measurements (BET and BJH methods) have been a powerful tool for characterization of nano or mesoporous material. Representative nitrogen adsorption-

30 desorption isotherms for the RH@[SiPrDABCO@BuSO₃H]HSO₄ are shown in Fig. 5. The surface area was determined by the BET method, whereas the pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) approach. The pore volume was calculated as the amount of liquid nitrogen adsorbed at P/P₀

35 = 0.979. The hysteresis loop was observed in the range of 0.4 < P/P₀ < 0.7, which is associated with capillary condensation taking place within the mesopores. The isotherms present a sharp adsorption step in the P/P₀, which implied that the material possess large pore size with narrow distributions. It shows

40 relatively low surface area (192 m² g⁻¹), compared with RH-SiO₂ that was reported by adam.³⁰ In addition, RH@[SiPrDABCO@BuSO₃H]HSO₄, exhibits pore-size distribution at 3.32 nm, that is smaller than that of RH-SiO₂ (10.4 nm). The characteristic data on the sample are summarized in

45 Table 1.

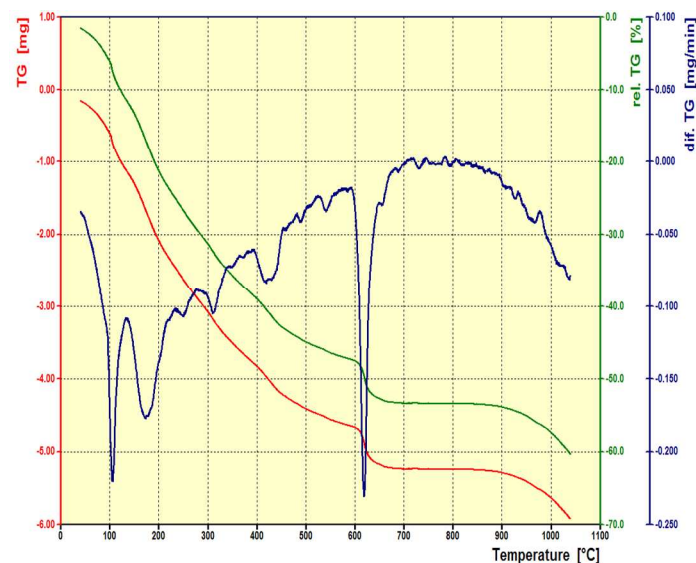


Fig. 4 TGA-DTG of RH@[SiPrDABCO@BuSO₃H]HSO₄

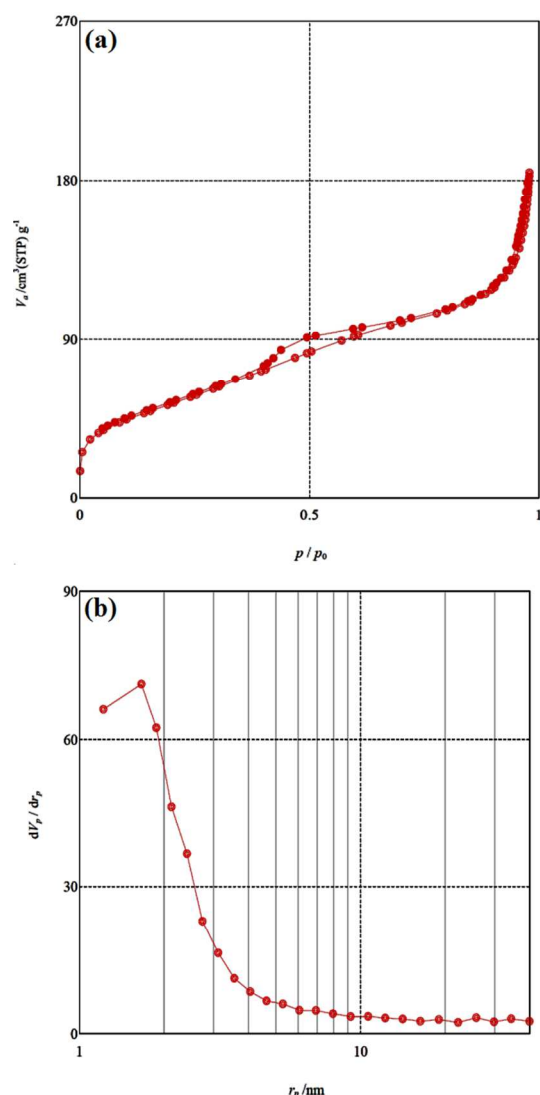


Fig. 5 (a) Pore size distributions and (b) Nitrogen adsorption-desorption isotherm of RH@[SiPrDABCO@BuSO₃H]HSO₄

Table 1 Specific surface area (S_{BET}), diameter pore and total pore volume.

Sample	BET surface area ($\text{m}^2 \text{g}^{-1}$)	diameter (nm)	pore volume ($\text{cm}^3 \text{g}^{-1}$)
Rice husk SiO ₂	347	10.4	0.872
RH@[SiPrDABCO@BuSO ₃ H]HSO ₄	192	3.32	0.285

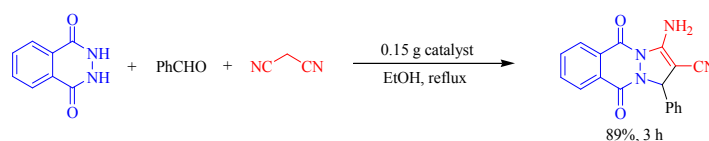
Application of RH@[SiPrDABCO@BuSO₃H]HSO₄ as Brönsted solid acid catalyst for one-pot synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones

To investigate the catalytic activity of RH@[SiPrDABCO@BuSO₃H]HSO₄ in the one-pot multicomponent synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione heterocyclic compounds, we focused on systematic evaluation of different conditions for the model three-component couplings of phthalhydrazide, benzaldehyde, and malononitrile (Scheme 2). Various amounts of catalyst, solvents and temperature, were screened to test the efficiency of the catalyst and the results are summarized in Table 2. As could be seen in

Table 2, the best result was obtained with a 0.15 g (6 mol%, H⁺) of RH@[SiPrDABCO@BuSO₃H]HSO₄ as the catalyst at reflux condition. Using lower amount of catalyst resulted in lower yields, while higher amount of catalyst did not affected reaction times and yields. To study the effect of temperature on this synthesis, it was observed that a lower reaction temperature leads to a lower yield. Table 2 demonstrates that ethanol was the best choice of solvent. It should be pointed out that in the absence of RH@[SiPrDABCO@BuSO₃H]HSO₄, the reaction was sluggish and even after prolonged reaction time a considerable amount of starting material was remained.

Different substituted 1H-pyrazolo[1,2-b]phthalazine-5,10-diones were prepared changing the aromatic aldehyde substituents (Scheme 3). Generally, the reactions that employed aromatic aldehydes bearing electron-withdrawing or electron-donating functional groups at different positions produced the corresponding products in good to excellent yields. Both of the aromatic aldehydes with electron-withdrawing and electron-donating functionalities were found to be compatible under the optimized reaction condition (Table 3).

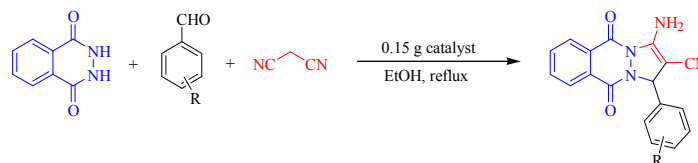
The structures of products were determined from their analytical and spectral (IR, ¹H & ¹³C NMR) data and by direct comparison with authentic samples. Formation of the products was also confirmed with the comparison of their melting points with the products prepared by reported methods.¹⁷⁻¹⁹



Scheme 2 Three component reaction of phthalhydrazide (1 mmol), malononitrile (1 mmol) and benzaldehyde (1 mmol)

Table 2 The one-pot three component reaction of phthalhydrazide (1 mmol), malononitrile (1 mmol) and benzaldehyde (1 mmol) under different conditions.

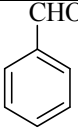
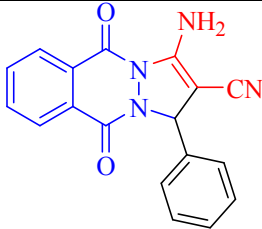
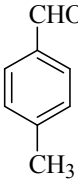
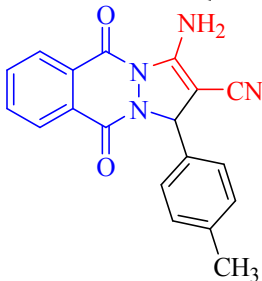
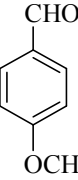
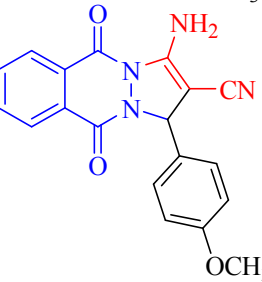
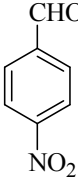
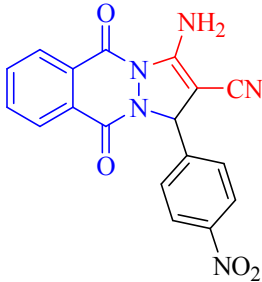
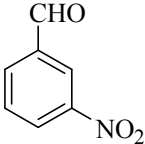
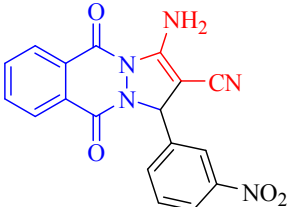
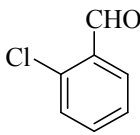
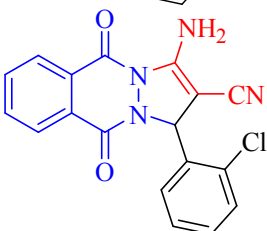
Entry	Solvent	Temperature (°C)	Catalyst (g)	Time (h)	Yield (%)
1	EtOH	Reflux	-	4	Trace
2	EtOH	30	0.15	3	50
3	EtOH	50	0.15	3	67
4	EtOH	Reflux	0.15	3	89
5	H ₂ O	Reflux	0.15	3.5	71
6	CH ₃ CN	Reflux	0.15	4	60
7	CH ₂ Cl ₂	Reflux	0.15	4	65
8	EtOH	Reflux	0.1	3	78
9	EtOH	Reflux	0.2	3	89

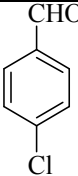
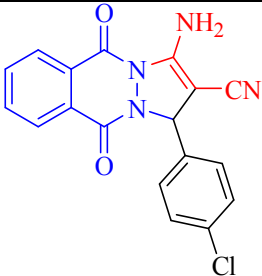
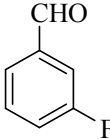
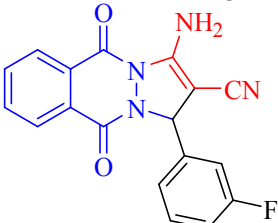
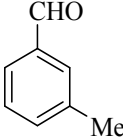
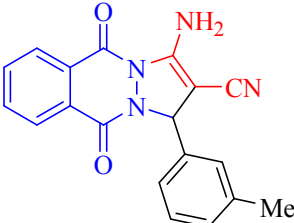
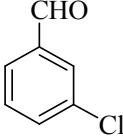
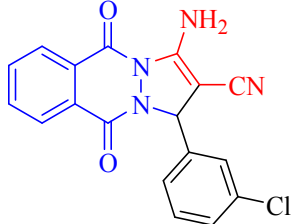
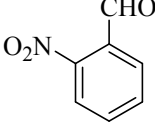
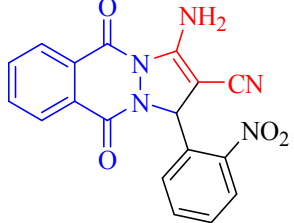
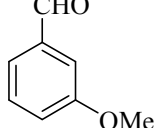
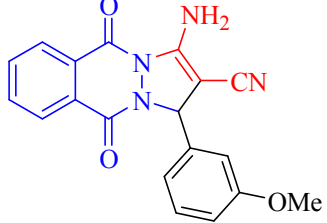


Scheme 3 Synthesis of different substituted 1H-pyrazolo[1,2-b]phthalazine-5,10-diones through multicomponent reaction promoted by

RH@[SiPrDABCO@BuSO₃H]HSO₄

Table 3 The one-pot three component synthesis of 1H-pyrazolo[1,2-]phthalazine-5,10-diones catalyzed by $\text{RH}@\text{[SiPrDABCO@BuSO}_3\text{H]HSO}_4$.

Entry	Aldehyde	Product	Time (h)	Yield (%)
a			3	89
b			4	86
c			5	84
d			3	94
e			3	91
f			4	88

g			3	92
h			4	87
i			4	86
j			3	88
k			4	90
l			4	86

The steric and electronic properties of the aldehydes affected the reaction yields. For example 4-nitrobenzaldehyde provided excellent yield of 94%. The para-substituted aldehydes gave good results compared to the ortho-substituents due to more steric hindrance for the ortho-substituted aldehydes on the product formation than the para-substituted aldehydes with the use of acidic catalysts.

To investigate the activity constancy of the catalyst, the catalyst was reused five in the one-pot multicomponent condensation of benzaldehyde, malononitrile and phthalhydrazide. The catalyst was recovered after each run, washed with hot ethanol, dried and tested for its activity in the subsequent run. The results were

shown that the catalyst does not show any loss in its activity and produced product in 89, 87, 87, 85 and 85 % yield, respectively.

3. Experimental

General

Chemical materials were purchased from Fluka and Merck companies and used without further purification. Rice husk (RH) was collected from a rice mill in Khuzestan-Baghmalek (Iran).

Products were characterized by comparison of their physical data, IR and ^1H NMR and ^{13}C NMR spectra with known samples. The purity determination of the products and reaction monitoring

were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. NMR spectra were recorded in CDCl_3 on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as internal standard. Fourier transmission infrared (FT-IR) spectra of the powders (as pellets in KBr) were recorded using a Fourier transmission infrared spectrometer (BOMEM MB-Series 1998 FT-IR spectrometer).

The TGA curve of the $\text{RH}@[\text{SiPrDABCO}@\text{BuSO}_3\text{H}]\text{HSO}_4$ was recorded on a Bahr, SPA 503 at heating rates of $10\text{ }^\circ\text{C min}^{-1}$.

The thermal behavior was studied by heating 1–5 mg of samples in aluminum-cripped pans under nitrogen gas flow, over the temperature range of 25–1000 $^\circ\text{C}$. X-ray diffraction (XRD) patterns of samples were taken on a Philips X-ray diffractometer Model PW 1840. The particle size and external morphology of the particles were characterized by scanning electron microscopy, SEM (Philips XL30 scanning electron microscope).

Extraction of silica from rice husk (RH-SiO₂)

Amorphous silica nanoparticles were prepared from low-cost rice husk (RH-SiO₂).³² Briefly, rice husk was washed with tap water and rinsed with distilled water to remove dirt. After drying at room temperature, the rice husk was stirred with 1.0 M nitric acid at room temperature for about 24 h. It was thoroughly washed with distilled water until the pH of the rinse became constant. The wet RH was subsequently dried in an oven at 100 $^\circ\text{C}$ for 24 h. The cleaned RH was burned in a muffle furnace at 800 $^\circ\text{C}$ for 6 h. Silica extraction from RH was carried out by stirring the rice husk in 500 mL, 1.0 M sodium hydroxide for 24 h at room temperature. Then the mixture was filtered to remove the undissolved residues. The extracted sodium silicate was titrated with 3.0 M HNO_3 . The acid solution was added at a slow rate of ca. 1.0 mL min^{-1} with constant stirring. Silica gel started to precipitate when the pH decreased to less than 10. The titration was continued until the solution pH reached 5.0. The silica gel/precipitate was aged for 24 h. The silica gel/precipitate was filtered, washed thoroughly with distilled water and dried at 100 $^\circ\text{C}$ for 18 h.

Synthesis of n-propyltrimethoxysilane-1,4-diazoniabicyclo[2.2.2]octane chloride-butylsulfonate, $\text{SiPrDABCO}@\text{BuSO}_3^-$

DABCO (0.897 g, 8.0 mmol) were dissolved in acetone (100 mL). To this solution 8 mmol of 3-chloropropyltrimethoxysilane, CPTMS (1.58 g), was added drop-wise and the mixture was refluxed for 24 h under N_2 atmosphere. The solvent was removed by rotary evaporation under reduced pressure and a white precipitate was obtained (SiPrDABCO). 1,4-Butane-sultone (1.09 g) was slowly added into the solution of equal-molar n-propyltrimethoxysilane-1,4-diazoniabicyclo[2.2.2]octane chloride (SiPrDABCO) and toluene (100 mL). The mixture was stirred at 100 $^\circ\text{C}$ for 12 h and toluene was removed by rotary evaporation under reduced pressure. The formed $\text{SiPrDABCO}@\text{BuSO}_3^-$ then was washed with ether for 3 times and dried in vacuum at 50 $^\circ\text{C}$ for 3 h.

Preparation of immobilized ionic liquid solid acid catalyst, $\text{RH}@[\text{SiPrDABCO}@\text{BuSO}_3\text{H}]\text{HSO}_4$

About 2.0 g of the nano silica (obtained from RHA) was stirred in 350 mL of 1.0 M NaOH at room temperature. The resulting

sodium silicate was titrated with 1.0 M HCl at a slow rate of ca. 1.0 mL min^{-1} with constant stirring until the solution pH reached 12. Then 2 g of $\text{SiPrDABCO}@\text{BuSO}_3^-$ was added and the resulting suspension was stirred at 100 $^\circ\text{C}$ for 8 h. The solution was then titrated slowly (1.0 mL min^{-1}) with 1.0 M HCl with constant stirring. The change in pH was monitored by using a pH meter. A gel started to form when the pH decreased to less than 10.0. The titration was done slowly until pH 5 was reached. The resulting suspension was stirred at 80 $^\circ\text{C}$ for 24 h and also reacted at 100 $^\circ\text{C}$ under static condition for another 24 h. The separation process was repeated 3 times with distilled water. The precipitate was filtered, subsequently washed with acetone, ether and ethanol. Finally, the formed immobilized acidic ionic liquid was dried in vacuum at 60 $^\circ\text{C}$ for 6 h. The formed solid was dissolved in 5 mL H_2O in a 250 mL round bottom flask, and sulfuric acid (0.43 mL, 8 mmol) was slowly dropped into the flask at 0 $^\circ\text{C}$. After the dropping was finished, the mixture was heated up to 60 $^\circ\text{C}$ gradually and then stirred for 12 h. The solid was filtered, subsequently washed with ethanol and water and then dried at room temperature.

Typical experimental procedure for the synthesis of phthalazine derivatives

A mixture of malononitrile (0.07 g, 1 mmol), aldehyde (1.1 mmol), phthalhydrazide (0.16 g, 1 mmol), and $\text{RH}@[\text{SiPrDABCO}@\text{BuSO}_3\text{H}]\text{HSO}_4$ (0.15 g) was refluxed in ethanol for the time shown in Table 3. Completion of the reaction was indicated by TLC. After completion of reaction, the reaction mixture was washed with hot ethanol and the catalyst was filtered. The crude product was purified by recrystallization in aqueous ethanol to afford the pure product.

pH-analysis of $\text{RH}@[\text{SiPrDABCO}@\text{BuSO}_3\text{H}]\text{HSO}_4$

To an aqueous solution of NaCl (1 M, 25 mL) with an initial pH 5.9, the $\text{RH}@[\text{SiPrDABCO}@\text{BuSO}_3\text{H}]\text{HSO}_4$ (100 mg) was added and the resulting mixture stirred for 24 h after which the pH of solution decreased to 2.8. This is equal to a loading of 0.4 mmol $\text{SO}_3\text{H/g}$ of acidic catalyst. Additionally, this result confirmed by back-titration analysis of the catalyst.

Conclusion

In this research, inorganic-organic hybrid Brønsted solid acid catalyst, $\text{RH}@[\text{SiPrDABCO}@\text{BuSO}_3\text{H}]\text{HSO}_4$, was successfully prepared through the supporting of acidic ionic liquid containing double-charged diazoniabi-cyclo[2.2.2]octane chloride onto the nano silica. The FT-IR, SEM, TGA-DTA, and BET were clearly shown that $[\text{SiPrDABCO}@\text{BuSO}_3\text{H}]\text{HSO}_4$ successfully immobilized on the surface of rice husk silica (RH-SiO₂) by chemical covalent bond. The catalytic activity of this solid acid nanocomposite, was probed through the one-pot synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones via three-component couplings of phthalhydrazide, aromatic aldehydes, and malononitrile. In this reactions $\text{RH}@[\text{SiPrDABCO}@\text{BuSO}_3\text{H}]\text{HSO}_4$ shows a highly catalytic nature, easy to handle procedure, easy workup, recycle exploitation, good to excellent isolated yields and the use of ethanol as a solvent that is a relatively environmentally benign solvent. Subsequent reuse of catalyst showed that the catalysis

was wholly heterogeneous.

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Notes and references

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- 1 J. Davarpanah, A. R. Kiasat., *RSC Adv.*, 2014, **4**, 4403.
- 2 A. R. Kiasat and S. Nazari., *Catal. Sci. Technol.*, 2012, **2**, 1056.
- 3 S. Safaei, I. Mohammadpoor-Baltork, A. R. khosropour, M. Moghadam, S. Tangestaninejad and V. Mirkhani, *Catal. Sci. Technol.*, 2013, **3**, 2717.
- 4 F. Adam, P. Retnam and A. Iqbal, *Appl. Catal., A: Gen.*, 2009, **357**, 93.
- 5 A. E. Ahmed and F. Adam, *Microporous Mesoporous Mater.*, 2009, **118**, 35.
- 6 F. Adam, K. Kandasamy and S. Balakrishnan, *J. Colloid Interface Sci.*, 2006, **304**, 137.
- 7 O. B. Shawkataly, R. Jothiramalingam, F. Adam, T. Radhika, T. M. Tsao and M. K. Wang, *Catal. Sci. Technol.*, 2012, **2**, 538.
- 8 J. Miao, H. Wan and G. Guan, *Catal. Commun.*, 2011, **12**, 353.
- 9 A. S. Amarasekara and O. S. Owereh, *Catal. Commun.*, 2010, **11**, 1072.
- 10 A. M. Mercet, R. Pleixats, X. Cattoen and M. W. C. Man, *Catal. Sci. Technol.*, 2011, **1**, 1544.
- 11 J. Miao, H. Wan, Y. Shao, G. Guan and B. Xu, *J. Mol. Catal. A: Chem.*, 2011, **348**, 77.
- 12 M. Z. Kassae, H. Masrouri and F. Movahedi, *Appl. Catal., A: Gen.*, 2011, **395**, 28.
- 13 Q. Zhang, H. Su, J. Luo and Y. Wei, *Green Chem.*, 2012, **14**, 201.
- 14 L. Gao, L. Bing, Z. Zhang, H. Kecheng, H. Xiaoyun and K. Deng, *J. Organomet. Chem.*, 2013, **735**, 26.
- 15 Q. Zhang, J. Luo and Y. Wei, *Green Chem.*, 2010, **12**, 2246.
- 16 Z. Chen, Q. Zhu and W. Su, *Tetrahedron Lett.*, 2011, **52**, 2601.
- 17 G. Karthikeyan and A. Pandurangan, *J. Mol. Catal. A: Chem.*, 2012, **361-362**, 58.
- 18 M. R. Nabid, S. J. Tabatabaei-Rezaei, R. Ghahremanzadeh and A. Bazgir, *Ultrason. Sonochem.*, 2010, **17**, 159.
- 19 S. H. Song, J. Zhong, Y. H. He and Z. Guan, *Tetrahedron Lett.*, 2012, **53**, 7075.
- 20 R. P. Jain and J. C. Vederas, *Bioorg. Med. Chem. Lett.*, 2004, **14**, 3655.
- 21 R. W. Carling, K. W. Moore, L. J. Street, D. Wild, C. Isted, P. D. Leeson, S. Thomas, D. O'Conner, R. M. McKernan, K. Quirk, S. M. Cook, J. R. Atack, K. A. Waftord, S. A. Thompson, G. R. Dawson, P. Ferris and J. L. Castro, *J. Med. Chem.*, 2004, **47**, 1807.
- 22 F. A. Assar, K. N. Zelenin, E. E. Lesiovskaia, I. P. Bezhan and B. A. Chakchir, *Pharm. Chem. J.*, 2002, **36**, 598.
- 23 G. Shanthy and P.T. Perumal, *J. Chem. Sci.*, 2010, **122**, 415.
- 24 X. Zhang, Y. Li and Z. Zhang, *Tetrahedron* 2011, **67**, 7426.
- 25 J. Wang, X. Bai, C. Xu, Y. Wang, W. Lin, Y. Zou and D. Shi, *Molecules* 2012, **17**, 8674.
- 26 H. Chen and D.Q. Shi, *J. Heterocycl. Chem.*, 2013, **50**, 56.
- 27 A. R. Kiasat, S. Noorizadeh, M. Ghahremani and S. J. Saghanejad, *J. Mol. Struct.*, 2013, **1036**, 216.
- 28 A. R. Kiasat and J. Davarpanah, *J. Mol. Catal. A: Chem.*, 2013, **373**, 46.
- 29 J. Davarpanah, A. R. Kiasat, S. Noorizadeh and M. Ghahremani, *J. Mol. Catal. A: Chem.*, 2013, **376**, 78.
- 30 A. R. Kiasat, A. Mouradzadegun and S. J. Saghanezhad, *J. Serb. Chem. Soc.*, 2013, **78**, 1.
- 31 F. Adam, H. Osman and K. M. Hello, *J. Colloid Interface Sci.*, 2009, **331**, 143.
- 32 F. Adam and A. Iqbal, *Chem. Eng. J.*, 2010, **160**, 742.