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Zirconium based porous coordination polymer (PCP) bearing organocatalytic

ligand: a promising dual catalytic center for ultrasonic heterocycle synthesis

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Abstract

Herein, the efficient role of ultrasonic irradiation both in synthesis of Zr based porous coordination polymer (Zr-PCP) nanoparticles and boosting its catalytic activity, towards the benzimidazoles synthesis is represented. We use an amine based ligand (amino-terephthalate) for PCP and we exhibit that it can have a synergistic catalytic activity. In this work, a unique nano-engineering of cooperative and synergistic catalytic activity of zirconium, as a Lewis acid, and aminophenylene, as an organocatalyst, in the synthesis of heterocycles is presented for the synthesis of benzimidazole from cascade reaction of phenylene diamine with aldehyde at ambient temperature. The catalyst shows Zr and amine groups of the Zr-PCP are active catalytic sites which in combination with the ultrasonic irradiation leads to a high selectivity and rapid catalytic production of benzylimidazoles. N₂ adsorption-desorption along with BJH analyses confirm the microporosity of the catalyst and recyclability shows that the catalyst is green and sustainable heterogeneous microporous catalyst.

Keywords: Ultrasound Irradiation; Zr-PCP-NH₂; Benzimidazole; Sonochemical Synthesis, Green Catalyst.

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1. Introduction

Nanoporous coordination polymers (PCP), nowadays, are important class of porous nanoarchitechtures providing a large opportunities to design advanced set of nanomaterials such as catalysts [1, 2], adsorbents [3], and sensors [4], drug carrier [5]. Incorporation of organocatalytic ligands is an interesting approach to design a hybrid bifunctional catalyst (metal as Lewis acid and ligand functional group such as organobase or organocatalyst) with porous and crystalline structures [6]. By varying metal and ligand, a wide variety of structures with different pore shapes, sizes, and functionalities [7] can be achievable. Synthetic procedure of these materials include different methods such as ball-milling [8], sonication [9] and solvothermal approaches [10-15]. Among PCPs, we selected a 3D octahedral Zr-based PCP (Zr-PCP), owing to its high chemical stability and interesting chemistry for our further catalytic investigations in this project. One of the convenient properties of Zr-PCP is the aqueous stability of this PCP which convert it to a an interesting candidate for catalytic heterocyclic organic molecules synthesis [16].

Benzimidazoles as *N*-rich heterocycles are important class of heterocyclic compounds [17] that show various biological activities including antineoplastic [18], antiprotozoal [19], antiproliferative [20], antimicrobial, anthelmintic [21], and antiulcer [22] activities. Besides, they can be used to synthesis of ionic liquid [23], liquid crystals [24] and carbine based organometallic catalysts [25]. Two procedures are popular for the 2-substituted benzimidazoles synthesis; (1) phenylenediamines coupling with carboxylic acids [26] and (2) a two-step method including oxidative dehydrogenation of aniline manufactured in situ from the phenylenediamines

condensation with aldehydes [27]. The first method involves acidic conditions and high temperatures. But the last method is mainly used owing to the availability of the reagents and aldehydes. Another protocol is the one-pot tandem preparation from alcohols accelerated by bifunctional catalysts, in which alcohol is in situ oxidized to aldehyde and then cyclocondensated with amines [28, 29]. But this process suffers from drastic conditions, hard work-up, low yield and using homogeneous catalysts that cannot be recovered. In this regard, using the heterogeneous catalysts for selective benzimidazole synthesis can be greatly favorable [30].

Ultrasonic technology has been proving to be a safe and energy saving procedure for organic synthesis, because of the physical and chemical changes through acoustic cavitation phenomena i.e. quick formation, development and crumble of unsteady bubbles in liquids. The resulting local temperature, pressure and very high cooling rates derive extraordinary properties into the sonicated solutions [31-35]. Dhopte *et al.* applied graphene oxide as a reusable heterogeneous catalyst for the nenzimidazole synthesis, under ultrasonication for 60 minutes. They reached the 2-substituted benzimidazole with the yield of 89%. They also found that 60 minutes of ultrasonication at 35 °C is much more effective than 3 hour of stirring at 60 °C [36]. Similarly, Ziarati *et al.* synthesized benzimidazole derivatives, under ultrasonication. They used nanostructured NiFe-xEu_xO₄ for accelerating reaction, that reused for five cycles [37].

Herein, we designed a bifunctional catalyst with environmentally benign, stable and affordable and reusable features for green benzimidazole synthesis. We exploited both metal and organosites for the sustainable synthesis of benzimidazoles. These agents not only have disruptive effect on the performance of each other, but also synergizes each other in the catalysis. Ultrasonic irradiation is the third function that acts as a synergistic agent in this catalytic process (Figure 1).



Figure 1: Schematic illustration for the Zr-PCP-NH₂ catalyzed benzimidazole synthesis.

2. Experimental section

2.1. Materials and instruments

Zirconium tetrachloride tetrahydrofuran complex (ZrCl₄. 4H₂O), 2-aminoterephthalic acid (NH₂-H₂BDC), terephthalic acid (H₂BDC), aldehydes and *o*-phenylenediamine (OPD) were obtained from Merck. The other materials were purchased from Sigma and Merck (Germany) and Fluka (Switzerland), which were used without further purification.

Fourier transform Infrared (FT-IR) spectra were obtained by a Shimadzu IR-460 spectrometer (Japan). Scanning Electron Microscopy (SEM) images were recorded by a Zeiss-DSM 960A microscope (Germany). The crystalline structure of the nanoparticles was examined by X-Ray Diffraction (XRD) instrument (Philips-PW1800 diffractometer (Germany)). The ultrasound irradiation was applied using a FAPAN 1200 UPS (Iran) with a wave of frequency 28 ± 1 kHz and power 100 W. Adsorption-desorption isotherms were obtained by BEL sorp-mini autosorb (Japan). NMR spectroscopy was performed on a Varian (300 MHz) Brucker (Germany). DT/TGA of PCP-NH₂ was recorded on a Netzsch STA449 under nitrogen atmosphere from 50 to 800 °C (Figure S3).

2.1. Synthesis of Zr-PCP-H

To synthesize Zr-PCPs with open metal centers, a mixture of zirconium chloride (1 mmol), hydrochloric acid (2 mL, 12 mol.L⁻¹) in 20 mL of dimethyl formamide (DMF) was sonicated for 10 min to obtain a transparent solution. Then, 2.1 mmol of terephthalic acid (for Zr-PCP-H synthesis) or aminoterephtalic acid (for Zr-PCP-NH₂ synthesis) were dissolved in 40 mL of DMF and added to the first solution. The mixture was sonicated for 30 min and it was transferred to a Teflon autoclave. The autoclave was placed in an oven at 80 °C for 24 h. After cooling down the mixture at ambient temperature, it was centrifuged and washed with anhydrous DMF and acetone, several times. The white solid was dried under vacuum.

2.2. Synthesis of benzimidazole derivatives

Benzaldehyde (2 mmol), OPD (1 mmol), the catalyst (0.02 g) were added to a 3 mL ethanol at room temperature and stirred for 4 h. After completion of the reaction (monitored by TLC, hexane:ethylacetate, 1:4, respectively), the reaction temperature was cooled downed to 0 °C to precipitate. Then, the precipitate was washed with water and dried. The crude product was recrystallized by ethanol to afford the final product. In another pot, the same reaction was done by ultrasound irradiation for 30 min.

For investigating the reusability of the catalyst after completion the reaction, the mixture was filtered and the Zr-PCP-NH₂ nanocatalyst was rinsed twice with ethyl acetate; the filtrate was dried and the solvent was vaporized under vacuum and was reused for the next run.

2.3. Spectral data of synthesized compounds

All compounds are known and are previously reported in the *literatures* [38, 39]. ¹H NMR and ¹³C NMR spectra data of the synthesized products were given in the *supporting information* and one case of the ¹H NMR and ¹³C NMR spectra was given in Figures S1 and S2, respectively.

3. Results and discussion

First, PCPs bearing different ligands including terephthalate and aminoterephtalate were synthesized. Zr-PCP-H and Zr-PCP-NH₂ [40-42]. The synthetic strategy is illustrated in Scheme 1. In this process, the synthetic details and hydrothermally factors have played a leading role. According to reports [43], the nature of the ligand and metal cluster contributes to the formation of porous structure and the chemical properties results in the porous structure.



Scheme 1. Schematic preparation of Zr-PCP-H and Zr-PCP-NH₂.

The chemical structure of the Zr-PCP-NH₂ and Zr-PCP-NH₂ were studied by Fourier transform infrared (FT-IR) spectrum (Figure 2). A broad band appeared at ~3000-3600 cm⁻¹ can be ascribed to stretching vibration of O-H bond of the carboxylic acids and amine moieties (3447 and 3366) of Zr-PCP-NH₂. The FT-IR spectra of the Zr-PCP-NH₂ and Zr-PCP-NH₂ also show Zr-O stretches at approximately 478 and 489 cm⁻¹. For Zr-PCP-NH₂, the strong peaks at 1386 cm⁻¹ symmetric and 1652 cm⁻¹ asymmetric vibration are corresponding to carboxylate presence in the PCP. The peaks at 1577 cm⁻¹ and 2923 cm⁻¹ are due to the stretching and bending vibrations

of the aromatic C=C bonds of aromatic ring and aliphatic C-H of coordinated DMF and C-H of aromatic rings.



Figure 2. FT-IR spectra of synthesized Zr-PCP-H (red) and Zr-PCP-NH₂ (blue).

Energy dispersive X-ray spectroscopy (EDX) analysis was carried out to determine the existing elemental composition of Zr-PCP-NH₂. It can be observed that Zr-PCP-NH₂ is composed of C, O, N and Zr elements and Z-PCP-H is devoid of any N atom (Figure 3a,b), which is in consistent with its structure where the Zr-cluster coordinates with 2-aminoterephthalate ligand [6]. According to the elemental analysis, the molar ratio of C:Zr:O is 5:0.6:1.4, respectively. Judging from the X-ray diffraction (XRD) patterns of Zr-PCP-NH₂ (Figure 3c) and Zr-PCP-H (Figure 3d), these PCPs have pseudo-crystalline structure, which are close to reported *literatures* [44].



Figure 3. EDX analyses of Zr-PCP-NH₂ and Zr-PCP-H, respectively (a, b), and XRD patterns of Zr-PCP-NH₂ and Zr-PCP-H, respectively (c, d).

Scanning electron microscopy SEM images of the Zr-PCP-NH₂ and Zr-PCP-H revealed that the synthesized PCP are in nanoparticle shapes (Figure 4a,b). Line and surface profiles of the planar area from the upside surface of Zr-PCP-NH₂ and Zr-NH are shown in Figure 4c-f, presenting the correspondence topography quantitatively.





Figure 4. SEM images of (a) Zr-PCP-NH₂ and (b) Zr-PCP-H. (c, e) Plot and surface profile of Zr-PCP-NH₂ and Zr-PCP-H. (d, f) Plot, and surface profile of Zr-PCP-NH₂ and Zr-PCP-H.

The BET specific surface areas of the prepared Zr-PCP-NH₂ and Zr-PCP-H were recorded by nitrogen adsorption-desorption isotherms at 77 K (Figure 5). The N₂ adsorption-desorption isotherms showing the surface areas of Zr-PCP-NH₂ and Zr-PCP-H as 396 and 415 m²/g, respectively, exhibiting that NH₂ induced an insignificant decrease on the surface area. Given the magnified shape, we can conclude that both isotherms follow type I, suggesting a microporous structure [45, 46]. The calculated pore volumes from t-plot for Zr-PCP-NH₂ and Zr-PCP-H were

0.33 and 0.38 cm³/g, respectively. These show that the substitution of amine groups has a minor influence on the pore organization. According to the BJH, both structures contain miscroporosity and they did not show any mesoporosity in the network (Figure S4).



Figure 5. N_2 adsorption-desorption isotherms of Zr-PCP-NH₂ (a) and its magnified (inset) and Zr-PCP-H (b and its magnified as (inset).

More recently, one-pot green and sustainable synthesis of biologically interest nitrogen-rich heterocyclic compounds with easy and commercially available materials has drawn increasing attention [47, 48]. After synthesis and characterization of Zr-PCP-H and Zr-PCP-NH₂, we applied them as catalysts for the ultrasonic assisted one-pot synthesis of benzimidazole heterocycle was investigated using mentioned catalysts as the bifunctional porous (Figure 6a). By applying each ratio of OPD and benzaldehyde, both mono- and di-substituted products are produced, but by applying different reaction conditions the products yields can be varied. To obtain the best reaction conditions, we used benzaldehyde (2 mmol), OPD (1 mmol) in ethanol, as the model reactants, by using 0.02 g of different catalysts i.e. Zr-PCP-H and Zr-PCP-NH₂ at

room temperature (Figure 6b). It was observed that the Zr-PCP-NH₂ yielded the highest conversation (Figure 6a). Therefore, the mixed ligands Zr-PCP-NH₂ was chosen as the best catalyst for the following steps.



Figure 6. Benzimidazole synthesis in the presence of Zr-PCP-H, Zr-PCP-NH₂ and Zr-PCP-NH₂-H (a). Ultrasonic assisted synthesis of mono- and di-substituted benzimidazoles by different OPD/benzimidazole ratios (b).

In the next step and in continuous of obtaining the best reaction conditions, the reaction was performed by using 0.02 g Zr-PCP-NH₂ catalyst. Two products with one and two substituents were obtained. It should be noticed that the reaction was performed once under high speed stirring (HSS) for 4 h (after 4 h, no significant change in the yield) and once again under ultrasound irradiation (US) for 30 min (after 30 min, no significant change in the yield). In each section, the results of these two conditions were given, separately. As shown in Table 1, the reaction conversion under the ultrasonication was higher than that under the high speed stirring. Another evidence of the improvement in reaction yield is seen from the change in the sonication length. By increasing the reaction time up to 30 min, the yield increased but further increase did not significantly affect the progression. The amount of catalyst influenced the reaction

conversion, and the higher conversion (98%) could be obtained with 0.02 g of Zr-PCP-NH₂ (entry 7). The solvent nature is also crucial for the BI synthesis. When the reaction was performed in water under HSS, insignificant amount of the products was obtained. By ultrasonication, the conversion increased by only 19% (entry 10). But, by applying toluene, dimethyl formamide (DMF), acetonitrile and ethanol as the solvent, the conversion increased that in ethanol, the highest conversion (~98%) was obtained (entry 13). The reaction conversion was reduced to 84%, when the temperature was increased to 70 °C (entry 17), therefore room temperature was chosen as the optimal temperature.

$\begin{array}{c} & & \\$								
	1112				H F ₁	Ph	F ₂	
	Conjustion	Catal			Conversion	Yield (%) ^[d]		
Entry	Sonication (min)	Catal.	Solvent	Temp. (°C)		F ₁	F ₂	
	(IIIII)	(g)			(031-3/1031-3)%	(US/HSS)	(US/HSS)	
1	15	0.02	EtOH	R. T.	92/85	58/52	34/33	
2	30	0.02	EtOH	R. T.	98/85	60/52	38/33	
3	45	0.02	EtOH	R. T.	98/85	60/52	38/33	
4	60	0.02	EtOH	R. T.	96/85	57/52	39/33	
5	30	0.005	EtOH	R. T.	90/70	54/42	36/28	
6	30	0.01	EtOH	R. T.	95/77	57/47	38/30	
7	30	0.02	EtOH	R. T.	98/85	60/52	38/33	
8	30	0.04	EtOH	R. T.	96/82	59/50	37/32	
9	30	0.08	EtOH	R. T.	95/80	59/50	36/30	
10	30	0.02	H ₂ O	R. T.	< 48/29	33/29	<15/Trace	
11	30	0.02	DMF	R. T.	73/55	47/37	26/18	
12	30	0.02	CH ₃ CN	R. T.	92/79	67/54	25/20	
13	30	0.02	EtOH	R. T.	98/85	60/52	38/33	
14	30	0.02	Toluene	R. T.	68/46	45/30	23/16	
15	30	0.02	EtOH	R. T.	98/85	60/52	38/33	
16	30	0.02	EtOH	50	87/76	52/46	35/30	
17	30	0.02	EtOH	70	84/68	51/41	33/27	

Table 1. Optimization of benzimidazole synthesis reaction conditions. [a]

^[a] Reaction conditions: Benzaldehyde (2 mmol), OPD (1 mmol), solvent: 3 mL in the presence of Zr-PCP-NH₂. ^[b] US: Under ultra-sonication (US).

^[c] HSS: Under high speed stirring (HSS) for 4 h.

^[d] Isolated yield.

With the optimal conditions in hand, then the scope of the reaction was investigated by using OPD and various benzaldehydes to yield the benzimidazole derivatives (Table 2). For all the

reaction, both mono- and di-substituted benzimidazole derivatives were obtained that can be due to the catalyst effect. With respect to Table 2, it was concluded that the electron-releasing substituents induce the di-substituted products and the electron-withdrawing substituents lead to the mono-substituted product. Also, steric hindrance in benzaldehyde derivatives has led to the reduction in the reaction conversion that can be due the nanoporous structure of the catalyst that hinders the bulky reactants entry.



Table 2. Synthesis of various benzimidazoles under HSS as well as US.^[a]

^[a] Reaction condition: Benzaldehyde (2 mmol), OPD (1 mmol), EtOH (3 mL) in the presence of Zr-PCP-NH₂ (0.02 g) and under US for 30 min or HSS for 4 hours.
^[b] Isolated yield.

The proposed mechanism for synergistic impact of catalyst in the synthesis of monosubstituted 2-benzimidazole is followed by (1) the coordination of OPD with zirconium of the Zr-PCP-NH₂ and simultaneous nucleophilic attack of the amine to the benzaldehyde, resulted in imine formation based on organocatalytic properties of $-NH_2$ group, (2) amine groups exchange. The coordinating the intermediate nitrogen of the OPD to the zirconium can stabilize it prevent it from reverse reaction. Continuing this process in the next step leads to cyclization of the intermediate and discarding the product from catalytic site by removing the linkage between amine of PCP-NH₂ and the reactant. After cyclization, the oxidation of produced ring in the presence of air O₂ leads to final product. Also, the second $-NH_2$ group of the OPD can react with the benzaldehyde that leads to the di-substituted product. The detailed mechanism was drawn in Scheme 2.



Scheme 2. Proposed mechanism for Zr-PCP-NH₂ catalyzed synthesis of benzimidazoles through bifunctional organocatalytic behavior.

For studying the catalyst recyclability, the synthesis reaction was performed by recovered Zr-PCP-NH₂ under the same condition as the first run. The catalyst was filtered, washed with ethyl acetate and methanol, dried under vacuum and reused for the next run. The reused catalyst yielded over 80% conversion after six runs (Figure 7a). The SEM image of the Zr-PCP-NH₂ after six times of recycling, illustrated that its surface morphology was almost retained (Figure 7b).





Figure 7. Reusability of the Zr-PCP-NH₂ for the benzimidazole synthesis and (a), its SEM image after six cycle (b).

We confirmed the bifunctional synergistic effect of catalyst by comparing the Zr-PCP-NH₂ with amine-less Zr-PCP-H and Zn-based metal organic framework of MOF-5. According to this comparison (Table 3), when we eliminate amine group from the catalyst structure, the catalytic activity has a remarkable decrease in the product yield, indicating the effective role of amine in the catalysis. On the other hand, when we replaced Zn^{2+} with Zr species, the catalyst's activity dropped. This can be ascribed to the prevailing catalytic activity of Zr to Zn metal ions. Besides, it conveys the catalytic role of Zr in synergizing the catalytic activity of Zr-PCP-NH₂.

Table 3. Comparison of the Zr-PCP-NH₂ with other catalysts for the BI synthesis. ^[a]



		(US/HSS)	F ₁ (US/HSS)	F ₂ (US/HSS)
1	Zn-BDC	55/40	32/25	23/15
2	NH ₂ -(CO ₂ Me) ₂ BDC	72/60	48/40	24/20
3	Aniline	40/37	30/23	20/14
4	Zr-PCP-NH ₂	98/85	60/52	38/33
5	Zr-PCP-H	75/60	55/43	33/25

^[a] Reaction condition: Benzaldehyde (2 mmol), OPD (1 mmol), EtOH: 3 mL in the presence of catalyst (0.02 g).

4. Conclusions

It showed that in porous coordination polymer, zirconium as an active Lewis acid site and aminophenylene, as an organobase, owing to their discrete localizations are compatible with each other and cause to synergistic catalytic activity in synthesis of heterocycles. On the other hand, due to the diffusion limitations, ultrasonic irradiation boosts the mass transfer and increase the reaction rate. Therefore, we achieved the benzimidazoles synthesis in a short reaction time, high yields and selectivity. Zr-PCP-NH₂ was efficiently recovered and reused at least for 6 times without significant decrease in reaction conversion exhibiting the reusability of the catalyst.

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Graphical abstract

Zirconium based porous coordination polymer (PCP) bearing organocatalytic ligand, a promising catalyst for heterocycle synthesis



Highlights

- > Zr-PCP-NH₂ was fabricated via ultrasonic irradiation as a fast and green method.
- > Zr-PCP with different functional moieties was used in BIM synthesis.
- > Zr-PCP-NH₂ showed higher catalytic activity than pristine Zr-PCP-H.
- > The catalyst is stable under the reaction conditions.

Zr-PCP-NH₂ can be reused multiple times without significant loss in its efficiency.