



# Polyionic liquid decorated chitosan beads as versatile metal-free catalysts for catalyzing chemical reactions in aqueous media

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## ABSTRACT

A new strategy is presented for enhancing the catalytic activity of cross-linked chitosan beads. More precisely, chitosan beads were cross linked with glutaraldehyde and then, vinyl functionalized. In the next step, the vinyl-functionalized beads were polymerized with the as-prepared 1-vinyl-3-butylimidazolium bromide to furnish polyionic liquid on beads. The resultant composite was subsequently utilized as a metal-free catalyst for catalyzing some classic organic transformations, including Knoevenagel condensation reaction and syntheses of tetrahydrobenzo[*b*]pyrans and pyrano[2,3-*d*]pyrimidines in aqueous media under mild reaction conditions. It was found that the novel composite could efficiently promote all of the examined reactions to afford the corresponding products in high yields. Moreover, the catalyst exhibited high recyclability for all reactions. The comparative studies also approved that the activity of the composite was superior compared to cross-linked bead and polyionic liquid.

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## 1. Introduction

Chitosan (CS) and CS beads have been extensively studied in various research domains. In fact, the availability and non-toxicity of CS [1,2] encouraged many scientists to apply this natural compound for developing biocompatible products, such as adsorbents, drug delivery systems and catalysts [3–7]. CS beads can be cross linked with classic cross-linking agents to furnish more robust beads [8]. On the other hand, abundant functional groups in CS beads facilitate their functionalization with different reagents.

Ionic liquids, ILs, are interesting thermally stable and low-toxic organic salts with extensive applications [9–11]. As ILs can be readily prepared and various organic cations and ions can be utilized for their fabrications [12–14], many ILs with diverse physiochemical properties can be devised [12,15,16]. In this regard, ILs with polymerized functionalities can be prepared and applied for the formation of poly ionic liquids, PILs. As, numerous IL functionalities are present in the backbone of PILs, it is expected that they exhibited superior properties compared to ILs in some applications, such as catalysis.

Pyrano [2,3-*d*]pyrimidines and tetrahydrobenzo[*b*]pyrans are important heterocyclic compounds that can be achieved via Knoevenagel condensation reaction [17–19]. As these organic compounds exhibited outstanding pharmaceutical and biological features, including antitumor, antihypertensive, antibacterial and anticancer activity [20–22], many efforts have been devoted to their efficient synthesis. As examples,

synthesis of pyrano [2,3-*d*]pyrimidines in the presence of ionic liquid [23–25], Brønsted acids [26–28] and magnetic catalysts [29,30] has been reported. Similarly, various heterogeneous catalysts, including magnetic and carbon supported catalysts have been developed for the synthesis of tetrahydrobenzo[*b*]pyrans [31–34]. However, some of the reported synthetic protocols have disadvantages, such as harsh reaction conditions, long reaction times, low yields, use of organic solvents, formation of by-products and wastes, and use of excess dosage of reagents or catalysts.

In the continuation of our attempt for coining catalytic composites with natural compounds [35–38], herein we wish to present a novel strategy for improving the catalytic activity of CS beads. In this regard, cross-linked CS beads were fabricated and vinyl-functionalized. Then, they have participated in polymerization reaction with 1-vinyl-3-butylimidazolium bromide to form PIL on CS beads. The resulting composite, CS-PIL, was applied as a metal-free catalyst for promoting Knoevenagel condensation reaction and syntheses of tetrahydrobenzo[*b*]pyrans and pyrano[2,3-*d*]pyrimidines in aqueous media under mild reaction conditions.

## 2. Experimental section

### 2.1. Chemical and reagents

Preparation of the catalyst was achieved by using the following chemicals: CS (Mw = 50,000–190,000, with deacetylation degree  $\geq 75\%$ , viscosity 20 cP for 1 wt%, in 1% acetic acid), glutaraldehyde (GA), 1-vinylimidazole (VIM), 2,2'-azobis (2-methylpropionitrile)

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(AIBN), 1-bromobutane, 3-(trimethoxysilane) propyl methacrylate (3-TMSPMA) and diethyl ether. The reagents used for the evaluation of the activity of the as-prepared catalyst included aldehyde, dimedone, malononitrile, barbituric acid, NaOH, MeOH and EtOH. All of the chemicals applied for this research were purchased from Sigma-Aldrich.

## 2.2. Apparatus and equipment

The techniques used for the validation of the catalyst structure included, Fourier transform infrared (FTIR), X-ray diffraction (XRD), Thermo gravimetric analysis (TGA), scanning electron microscope (SEM) and Energy dispersive spectroscopy (EDS). Chemical structure of the samples were identified using FTIR spectroscopy with PERKIN-ELMER-Spectrum 65. Siemens, D5000 apparatus via Cu K $\alpha$  source was utilized for analysis of the structure of the catalyst. The thermal features of the samples were determined by TGA on METTLER TOLEDO at a heating rate of 10 °C.min<sup>-1</sup> under N<sub>2</sub> flow. The morphology and composition of Bead-PIL were explored via JMIRA 3 TESCAN-XMU.

## 2.3. Preparation of bead-PIL

### 2.3.1. Synthesis of IL

IL monomer was prepared via a solvent-free procedure [39]. In this respect, VIM (5 mL) and excess amount of 1-bromobutane were charged in a reaction vessel and stirred at 70 °C for 1 day under inert atmosphere. Afterward, the resulting mixture was cooled. Then, diethyl ether was added to obtain viscous IL. At the end, diethyl ether was removed under vacuum and the resultant IL was washed with MeOH and dried at 40 °C overnight.

### 2.3.2. Synthesis of CS bead

Preparation of CS bead was achieved through conventional method [40]. Briefly, a solution of CS (2 g) in acetic acid solution (2%, 100 mL) was gently dropped via burette into aqueous solution of NaOH (0.5 M) to generate CS beads. Then, the generated beads were kept for 1 day in NaOH solution and washed with distilled water.

### 2.3.3. Synthesis of cross-linked bead

Cross linking of the formed beads was performed by treating them with GA solution in EtOH (5 wt%) under stirring condition. The reaction was continued at 70 °C for 12 h. Subsequently, the obtained beads, Bead-GAs, were separated, washed with EtOH and dried under vacuum.

### 2.3.4. Synthesis of bead-GA-V

In order to vinyl-functionalize Bead-GA, a mixture of Bead-GA (1.5 g) and 3-TMSPMA (1 mL) in EtOH (50 mL) was prepared and heated at 110 °C. Then, the reaction mixture was refluxed for 1 day under inert atmosphere. At the end, the obtained Bead-GA-V was separated, washed with MeOH and dried at ambient temperature overnight.

### 2.3.5. Synthesis of bead-PIL

Bead-PIL was synthesized via free-radical polymerization of the IL monomer and Bead-GA-V. Typically, Bead-GA-V (1 g) was suspended in EtOH and stirred for 30 min. In the following, a solution of IL monomer (1.5 g) and AIBN (0.1 g) was injected into above-mentioned mixture. The polymerization reaction was carried out at 70 °C for 1 day under inert atmosphere. At the end, Bead-PIL was collected, washed with MeOH and dried at ambient temperature. The procedure for the preparation of Bead-PIL is depicted in Fig. 1.

## 2.4. Evaluation of the catalyst activity

### 2.4.1. Knoevenagel condensation reaction

Aldehyde (1 mmol) and malononitrile (1.2 mmol) were mixed in H<sub>2</sub>O (10 mL). Then, Bead-PIL (10 mg) was added and the mixture was stirred at 25 °C for 30 min. The reaction progress was monitored by

thin-layer chromatography (TLC). After the reaction was completed, the solvent was removed and the product was recrystallized in EtOH, Fig. 2.

### 2.4.2. Synthesis of tetrahydrobenzo[b]pyran derivatives

A mixture of malononitrile (1 mmol), dimedone (1 mmol), aldehyde (1 mmol) and Bead-PIL as catalyst (20 mg) was stirred at 25 °C in H<sub>2</sub>O (15 mL) as solvent for 40 min. The reaction progress was followed using TLC, Fig. 2. Afterward, Bead-PIL was separated, washed with MeOH (3 × 10 mL) and dried for further use. The products were recrystallized in EtOH and purified via column chromatography.

### 2.4.3. Synthesis of pyrano[2,3-d]pyrimidine derivatives

A mixture of aldehyde (1 mmol), barbituric acid (1 mmol) and malononitrile (1 mmol) were added to a round-bottomed flask containing Bead-PIL (20 mg) and H<sub>2</sub>O (15 mL). The resulting mixture was stirred at room temperature for 20 min, Fig. 2. After completion of the reaction (as monitored by TLC), Bead-PIL was removed, washed with MeOH and derided for further use. The pure products were obtained after recrystallization in EtOH and purification via column chromatography.

## 3. Result and discussion

### 3.1. Bead-PIL characterization

According to visual observation, Bead exhibited spherical morphology. To further analyze the morphology and surface characterization of Bead, it was subjected to SEM analysis. As depicted in Fig. 3, the as-prepared Bead showed a smooth surface. The study of the morphology of Bead-PIL, Fig. 3, on the other hand, confirmed that upon introduction of PIL on Bead, it preserved its spherical morphology. However, the surface of Bead-PIL is rough and porous. This observation approved that conjugation of PIL caused morphological change.

To further evaluate Bead-PIL, EDS and elemental mapping analyses were also accomplished. The result of EDS analysis, presented in Fig. 4, indicated the presence of C, O, N, Br and Si atoms in Bead-PIL. C, N and O atoms can be attributed to Bead. On the other hand, C, N and Br atoms can approve conjugation of PIL. Moreover, attachment of 3-TMSPMA can be confirmed by observing Si atom in the composition of Bead-PIL.

FTIR spectroscopy was carried out for Bead, Bead-GA, Bead-GA-V, Bead-PIL samples, Fig. 5. The FTIR spectrum of the synthesized Bead is in good accordance with the literature [41] and exhibited the absorbance bands at 1058 cm<sup>-1</sup> (stretching of C—O group), 2921 cm<sup>-1</sup> (—C—H functionality), 3433 cm<sup>-1</sup> (amino and hydroxyl groups), and 1636 cm<sup>-1</sup> (N—H bending vibration and stretching for primary amine). Next, Bead-GA has been analyzed by FTIR spectroscopy. The FTIR spectrum of Bead-GA, shown in Fig. 5, possessed all of the above-mentioned absorbance bands related to Bead. This issue confirms the stability of Bead in the course of cross linking. In this spectrum, the sharp absorbance band in 1562–1702 cm<sup>-1</sup> can be indicative of formation of —C=N bonds. In the case of Bead-GA-V, the distinguishing absorbance band appeared at 1720 cm<sup>-1</sup>. This sharp band can be assigned to the —C=O functionality in 3-TMSPMA. Moreover, the broad band at 1041–1190 cm<sup>-1</sup> can be attributed not only to the stretching of C—O group, but also to the —Si—O functionality of 3-TMSPMA. In the FTIR spectrum of the catalyst, the absorbance bands of Bead-GA-V can be observed. Noteworthy, the characteristic bands of PIL, i.e. —C=N bonds of the imidazolium rings overlap with imine bands resulted from cross linking with GA.

Thermograms of Bead, Bead-GA, Bead-GA-V and Bead-PIL are depicted in Fig. 6. As can be observed, Bead thermal stability is low and degradation of Bead was discerned at 250 °C. Bead-GA-V thermogram showed that the thermal stability of this sample is higher than that of Bead. This issue is expectable, as the cross-linked network in

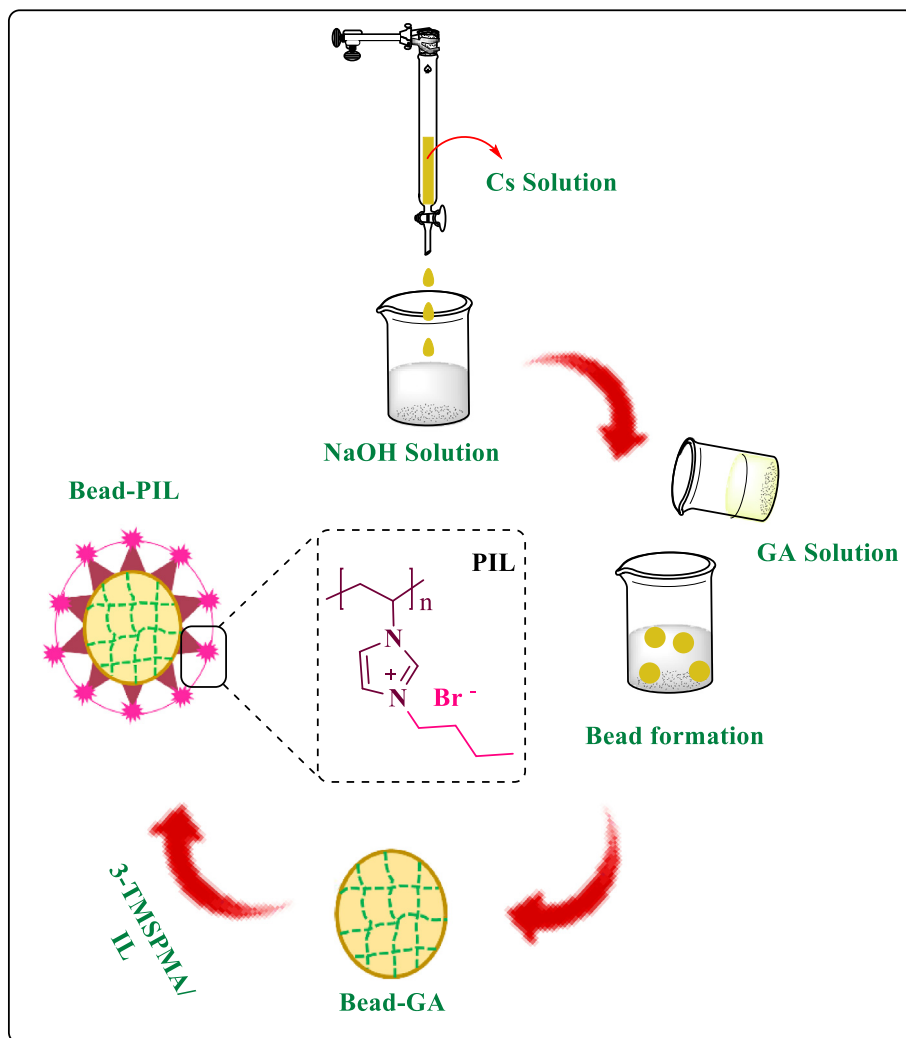


Fig. 1. Schematic illustration of Bead-PIL preparation.

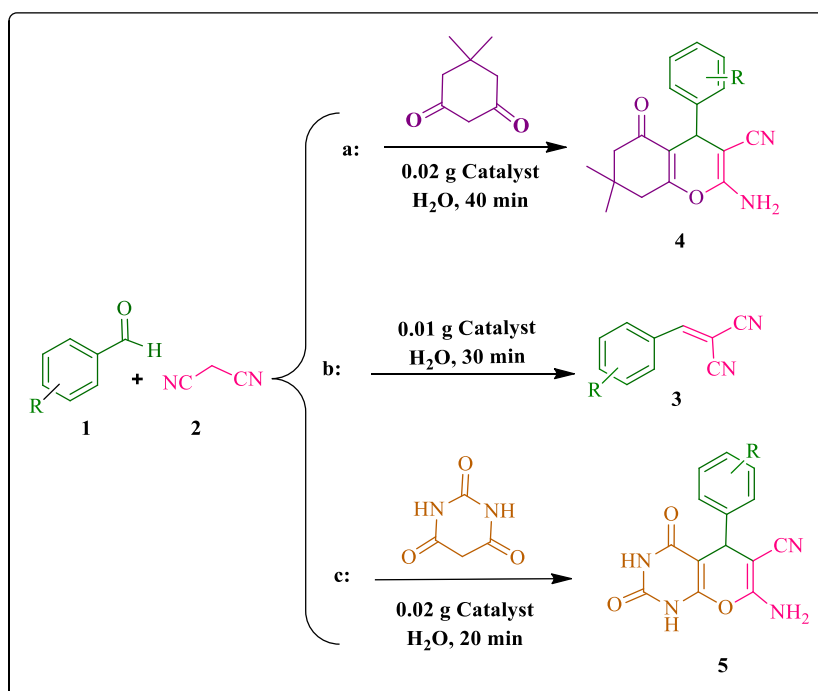


Fig. 2. a: Knoevenagel reaction, b: synthesis of tetrahydrobenzo[b]pyran and c: synthesis of pyrano[2,3-d]pyrimidine by using Bead-PIL as catalyst.



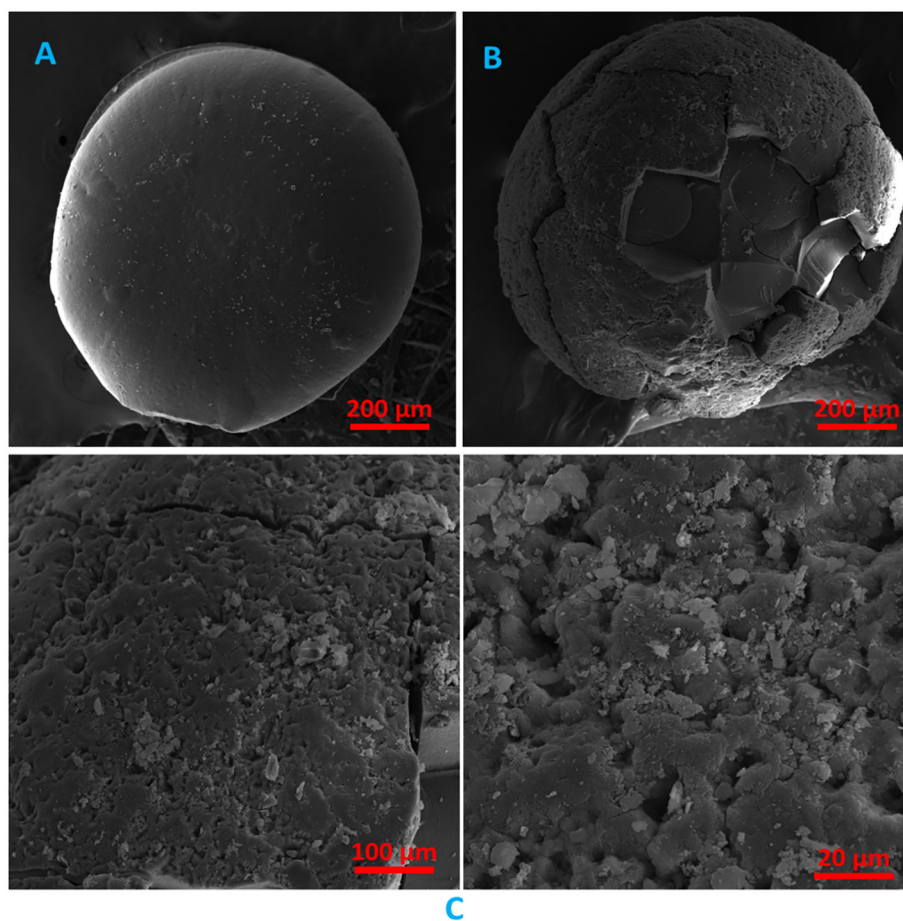


Fig. 3. SEM images of A: Bead, B and C: Bead-PIL.

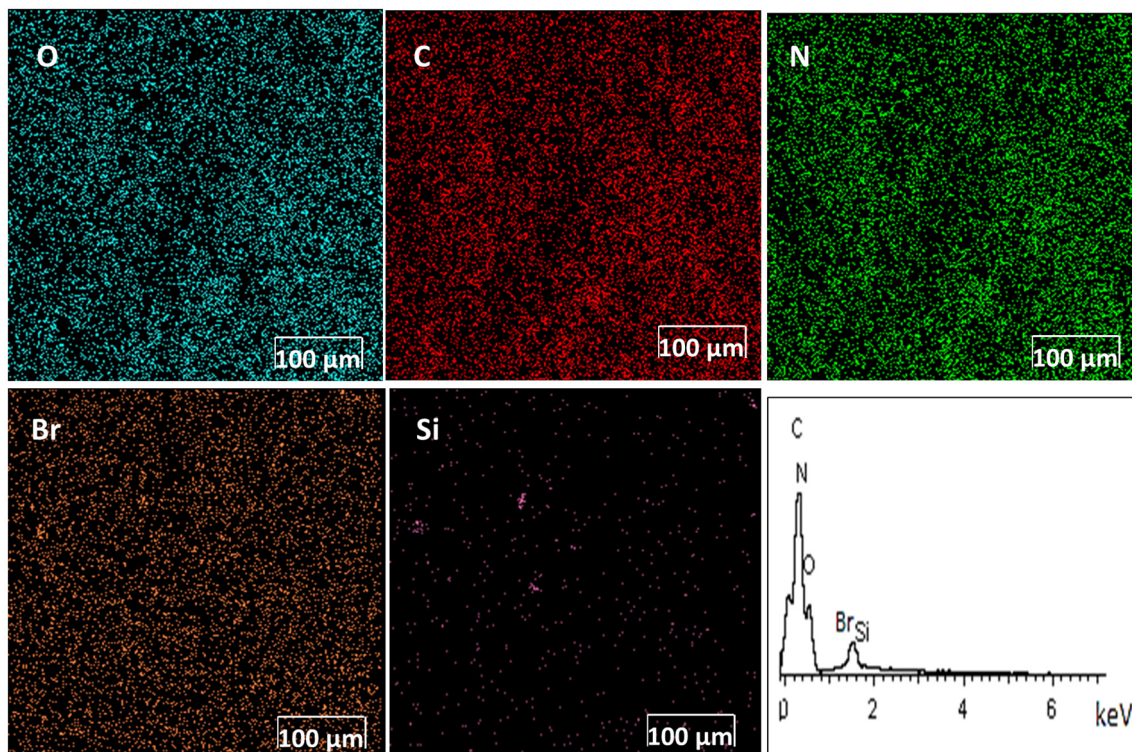


Fig. 4. Elemental mapping and EDS analyses of Bead-PIL.

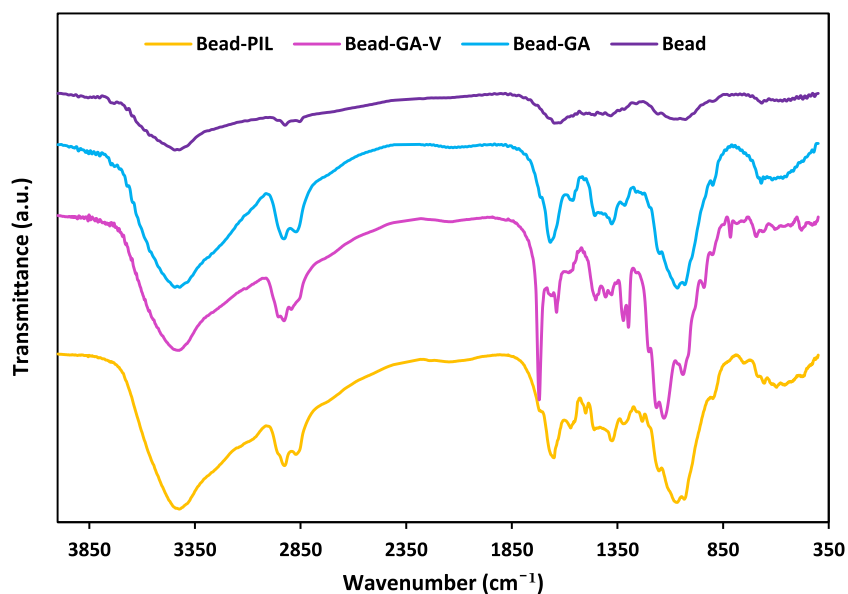


Fig. 5. FTIR spectra of Bead, Bead-GA, Bead-GA-V, Bead-PIL.

Bead-GA-V improved its thermal stability. In fact, in this sample apart from the weight loss at 250 °C, another weight loss at 430 °C can be observed. In the thermogram of Bead-PIL, two main weight losses appeared at 280 °C and 450 °C. These weight losses can be attributed to the degradation of Bead-GA-V and PIL.

XRD analysis of Bead-PIL, Fig. S1, indicated its amorphous structure. This issue is in good accordance to the literature [42].

### 3.2. Catalyst activity

Catalytic activity of CS and CS Bead for promoting organic reactions has been proved previously [43]. On the other hand, the potential of ILs and PILs as metal-free catalysts has been extensively

studied [44]. In attempt to improve the activity of Bead and benefiting from the features of both Bead and PIL, in this research, cross-linked Bead has been covalently adorned with PIL. It was postulated that the resulting composite, Bead-PIL, exhibits high catalytic performance. In this respect, the catalytic activity of Bead-PIL for model Knoevenagel reaction of benzaldehyde and malononitrile was appraised. Gratifyingly, it was found that scant amount of Bead-PIL (0.01 g) could catalyze the reaction in aqueous media to give quantitative yield in 30 min. Next, the reliability of this procedure was validated by employing various aldehydes. It was found that not only benzaldehyde as a substrate led to excellent yield of the reaction, but also other aldehydes with electron donating and electron withdrawing groups could also undergo this reaction to furnish high

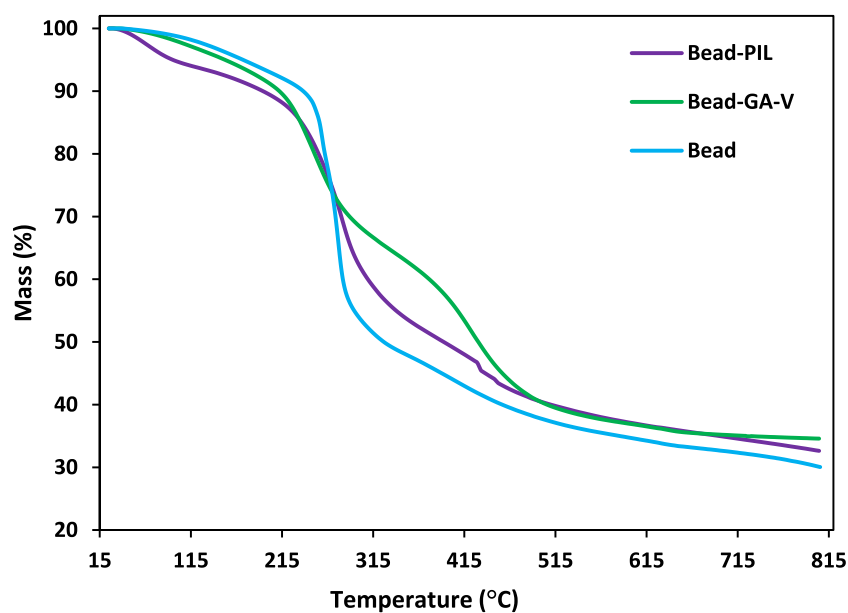
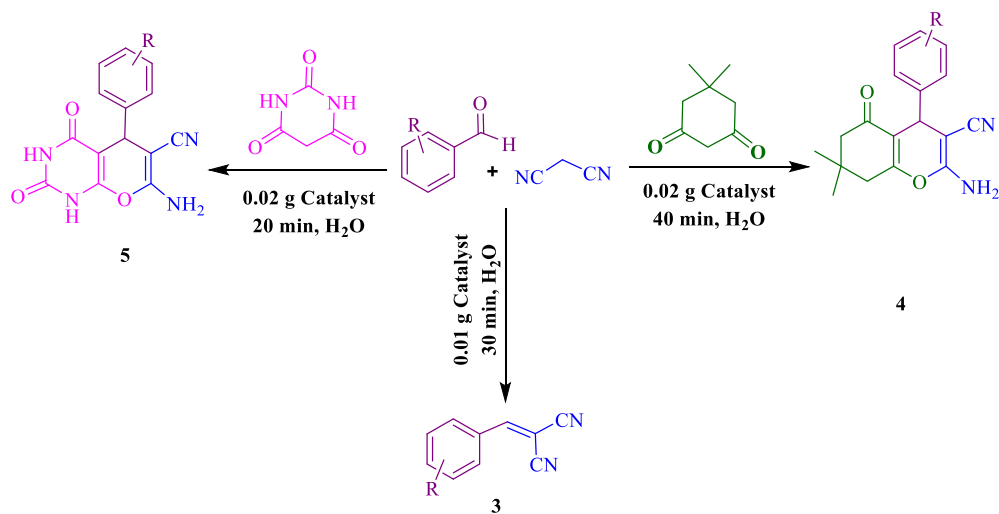


Fig. 6. Thermograms of Bead, Bead-GA-V, Bead-PIL.

yields of the corresponding products, Table 1. Next, to elucidate whether Bead-PIL could be utilized for other chemical reactions, performance of the catalyst for two one-pot, multi-component reactions, synthesis of tetrahydrobenzo[*b*]pyrans and pyrano[2,3-*d*]pyrimidines, was appraised. The results, Table 1, confirmed that

Bead-PIL could effectively promote both reactions. In fact, using very low dosages of the catalyst (0.02 g) the reactions proceeded to furnish high yields of the corresponding products in short reaction time, Table 1. These results affirmed that Bead-PIL is a versatile catalyst and can potentially promote various chemical transformations.

**Table 1**  
Knoevenagel reaction and synthesis of tetrahydrobenzo[*b*]pyran and pyrano[2,3-*d*]pyrimidine derivatives via Bead-PIL as catalyst .



Entry	Substrate	Products		
		(3) Yield %	(4) Yield %	(5) Yield %
1		100	97	100
2		97	90	95
3		100	95	100
4		95	90	95
5		98	95	95
6		90	90	95
7		90	85	90

**Table 2**

Comparison of the activities of control samples for the synthesis of the model pyrano[2,3-*d*]pyrimidine from one-pot reaction of benzaldehyde, barbituric acid and malononitrile under optimum reaction condition.

Entry	Sample	Yield (%)
1	Bead-PIL	100
2	PIL	80
3	Bead-GA-V	50
4	Bead-GA	50
5	Non-cross-linked bead	57
6	Bead + PIL <sup>a</sup>	87

<sup>a</sup> In this test, the physical mixture of PIL and Bead has been used as a catalyst, using the data derived from TG analysis of Bead-PIL, the ratio of PIL: Bead was determined.

### 3.3. Comparative study to disclose the roles of composite components in the catalysis

In the following, to elucidate the roles of Bead-PIL composite in the catalysis, a comparative experiment has been performed. In more detail, the catalytic performances of non-cross-linked bead, Bead-GA, Bead-GA-V, PIL, mixture of Bead and PIL and Bead-PIL for the synthesis of model pyrano[2,3-*d*]pyrimidine from one-pot reaction of benzaldehyde, barbituric acid and malononitrile were compared under similar reaction condition (Table 2). As listed in Table 2, the catalytic activity of non-cross-linked bead was moderate and led to the formation of

the model product in 57% yield. The observed catalytic activity of this sample can be assigned to the presence of the hydroxyl and amino functionalities of chitosan that activated the carbonyl group of the aldehyde and promoted the reaction. The catalytic activity of Bead-GA was also moderate and slightly lower than that of non-cross-linked bead. Similarly, functional groups of the Bead are responsible for the observed activity. Moreover, as some amino groups have been engaged in the condensation reaction with GA, the activity of this sample was slightly lower than that of non-cross-linked bead. The catalytic activity of Bead-GA-V was similar to that of Bead-GA. This result was expectable as low loading of 3-TMSPMA that was not catalytically active could not affect the catalytic activity. Examining the activity of PIL, on the other hand, established that this control catalyst showed good catalytic activity and 80% yield was furnished. High activity of this control catalyst is attributed to the presence of numerous ILs that are catalytically active species in the backbone of PILs. Interestingly, conjugation of Bead-GA-V and PIL resulted in a composite with activity superior to that of PIL and Bead-GA-V. In this sample, both ILs in the structure of PIL and Bead-GA-V functionalities participated in the catalysis. As a final control test, the model reaction has been conducted in the presence of Bead and PIL. For the sake of comparison, the ratio of PIL: Bead was selected as the same of that of Bead-PIL. In more detail, the TG analysis of the catalyst showed that that the content of PIL in Bead-PIL was 10 wt%. Hence, the similar ratio was selected for the control test, in which Bead and PIL were not covalently conjugated. The results

**Table 3**

Comparison of the activity of Bead-PIL with some of the reported catalysts for the synthesis of model pyrano[2,3-*d*]pyrimidine.

NO.	Catalyst	Catalyst amount	Solvent	Time (min)	Condition	Yield (%)	Ref
1	Bead-PIL	20 mg	H <sub>2</sub> O	30	Stirred, 25 °C	100	This Work
2 <sup>a</sup>	Fe <sub>3</sub> O <sub>4</sub> @PVA-Cu NPs	35 mg	H <sub>2</sub> O	10	Stirred/ 25 °C	95	[45]
3 <sup>b</sup>	CoFe <sub>2</sub> O <sub>4</sub> @Glutamine-Pr	40 mg	H <sub>2</sub> O	15	Stirred/ 25 °C	95	[46]
4 <sup>c</sup>	[TPPHSP]Br	2 mol%	H <sub>2</sub> O/EtOH	70	Reflux	80	[24]
5	liquid glass	25 mol%	H <sub>2</sub> O	60	Reflux	93	[47]
6 <sup>d</sup>	DBA	20 mol%	EtOH	58	Reflux	94	[48]
7	Mn-ZIF-8@ZnTiO <sub>3</sub>	0.06 mmol	H <sub>2</sub> O/EtOH	13	70 °C	95	[49]

[a] Fe<sub>3</sub>O<sub>4</sub>@polyvinyl alcohol magnetic nanoparticles, [b] immobilization of Praseodymium (Pr) Complexes on the surface of CoFe<sub>2</sub>O<sub>4</sub>, [c] triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide, [d] dibutylamine.

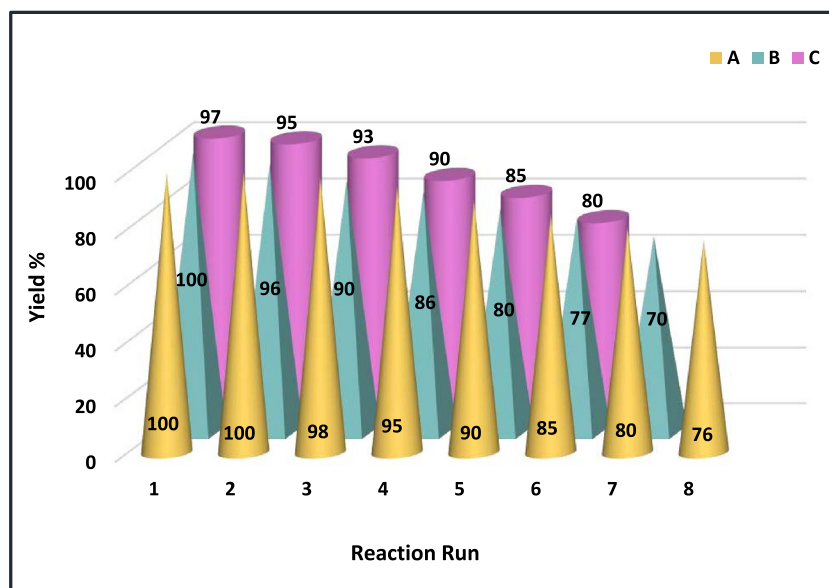
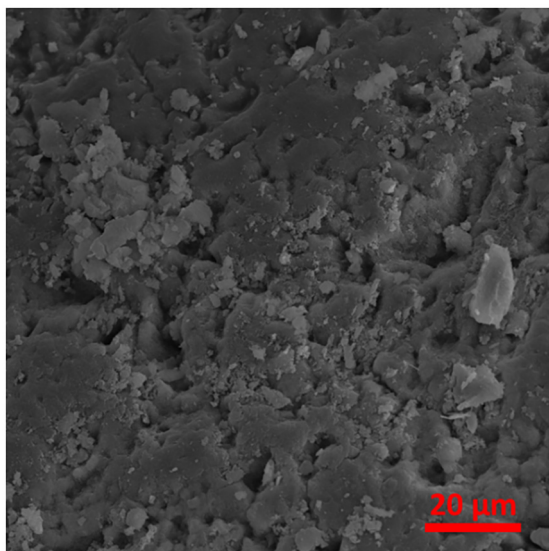


Fig. 7. Reusability of Bead-PIL for the synthesis of model products A: 3, B: 5, C: 4.





**Fig. 8.** SEM image of the recycled catalyst after eight runs for the model Knoevenagel condensation reaction.

confirmed that the activity of this catalytic system was lower than that of Bead-PIL. This issue can be ascribed to the synergistic effects between PIL and Bead.

### 3.4. Comparative study

As the results approved, Bead-PIL actively catalyzed some typical chemical transformations. To further disclose the potential of this metal-free catalyst, the performance of Bead-PIL for catalyzing synthesis of the model pyrano[2,3-*d*]pyrimidine was compared with some other catalysts. The summary of this comparison is presented in Table 3. As shown, the catalytic activity of Bead-PIL is comparative or superior to the tabulated catalysts. Regarding the reaction condition, it can be inferred that similar to the reported procedures, the reaction condition for Bead-PIL is also moderate. Comparing to homogeneous catalysts, Bead-PIL benefits from facile recovery and efficient recyclability. On the other hand, compared to some cases, in which synthesis of the catalyst required accurate procedures, synthesis of Bead-PIL can be achieved in a very simple way. Moreover, the metal-free nature of Bead-PIL is appealing from environmental aspects.

### 3.5. Catalyst recyclability

Bead-PIL recyclability was also examined. In this respect, the catalyst was separated at the end of all three model reactions (products achieved from benzaldehyde, barbituric acid and malononitrile) and after recovery, reused for the successive runs of the same reactions. As the results of this study indicated, Bead-PIL could potentially be reused for several runs of the model reactions with slight decrease of its activity after each run. Moreover, it was found out that the recyclability of the catalyst for Knoevenagel reaction was the highest. In more detail, in the case of the model compound 3, Bead-PIL could be used for eight successive runs and the yield of the product decreased from 100% (the first run) to 76% (the eighth run). In the case of compound 5, the decrease of reaction yield after seven run was 30%, while for the model compound 4, reuse of Bead-PIL for six runs led to 20% loss of the catalytic activity. (See Fig. 7.)

To appraise whether reusing of Bead-PIL incite morphological change, the reused catalyst after eight runs of the model Knoevenagel condensation reaction was analyzed by SEM, Fig. 8. As shown, this image is very similar to the SEM image of fresh Bead-PIL (see Fig. 3),

implying that upon several reuse of the catalyst, no significant morphological change occurred.

## 4. Conclusion

To benefit from the features of PIL and Bead, a covalent composite was fabricated through polymerization of Bead-GA-V and the as-prepared IL. The activity of the obtained composite, Bead-PIL, was examined for three classic organic reactions, i.e., Knoevenagel condensation reaction and syntheses of tetrahydrobenzo[*b*]pyrans and pyrano[2,3-*d*]pyrimidines in aqueous media under mild reaction conditions. The results showed that the catalyst could promote all of the discussed reactions efficiently. On the other hand, Bead-PIL exhibited good recyclability and could be reused for several runs. The comparison of the activity of Bead-PIL with that of PIL and Bead-GA-V also approved the superior activity of the former. This result confirms that incorporation of PIL on Bead-GA-V was beneficial for catalytic activity.

## Author statement

Samahe Sadjadi: Conceptualization; Funding acquisition; Project administration; Resources; Supervision; Writing - review & editing  
Fateme Koohestani: Formal analysis; Data curation; Methodology; Visualization; Investigation; Writing - original draft.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2021.115754>.

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