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Copper Loaded Cross-Linked Poly(Ionic Liquid): Robust Heterogeneous Catalyst in ppm Amount

Ali Pourjavadi,*[a] Seyed Hassan Hosseini,[a] Firouz Matloubi Moghaddam,[b] Seyed Ebrahim Ayati[b]

[a] *Polymer Research Laboratory, Department of Chemistry, Sharif University of Technology, Tehran, Iran*

[b] *Laboratory of Organic Synthesis and Natural Products, Department of Chemistry, Sharif University of Technology, Tehran, Iran*

(E-mail address: purjavad@sharif.edu; Phone/fax: (982)166165311)

Abstract

A novel heterogeneous copper catalyst was synthesized in which poly(1-vinyl imidazole-co-ionic liquid) was used as solid heterogeneous support. The catalyst was readily synthesized in a large scale amount. The catalyst has high loading level of copper ion and can be used in low weight percent. The resulted catalyst was highly active in the preparation of triazoles by Huisgen 1,3-dipolar cycloaddition method. In some cases the catalytic turnover number and frequency reached to 70002 and 3889 h^{-1}, respectively. The catalyst was recycled many times without significant loss of activity.

Keywords: Poly(ionic liquid), Heterogeneous catalyst, Copper catalyst, Huisgen cycloaddition

Introduction

After introducing the concept of "click chemistry" by Sharpless and co-workers in 2001, the copper catalyzed reaction of azides with alkynes to produce 1,2,3-triazoles has become the most reported reaction known as click reaction.[1-4] It was found that several members of 1,2,3-triazole family have biological and pharmaceutical properties.[5-7] Also, because of the mild reaction condition and high efficiency in the synthesis of 1,2,3-triazoles, these compounds are widely used in materials science.[8,9] The uncatalyzed reactions of alkynes and azides, known as Huisgen cycloaddition,[10] are strongly thermodynamically favored due to the high potential-energy content of the substrates, but have a relatively high kinetic-energy barrier which led to the very slow reaction and poor yield at room temperature.[11] Copper (I) catalyzes the reaction of terminal alkynes and azides and dramatically accelerates the reaction rates and produces 1,2,3-triazoles in high yields under mild reaction conditions.[12,13] However, the recovery of homogenous copper complexes after completion of the reaction is too difficult. Since, removal of trace amount of metal contamination from the products is essential, especially in pharmaceutical industry, copper catalysts should be completely separated from the products. Even with the extensive methods removal of trace amount of copper catalysts from the products remains a challenge. To solve the catalyst separation problem a rational approach is heterogenizing the homogenous catalysts. Several solid materials have been used for immobilization of copper complexes such as nanosilica,[14-16] mesoporous silica,[17,18] magnetic nanoparticle,[18-22] zeolite,[23,24] Alumina.[25] However, immobilization of copper complexes onto these solid materials suffers from some disadvantages such as multiple tedious steps for preparation of support surface, low loading of copper ion onto the surface of support material, low activity of catalyst after immobilization, high catalyst leaching and low thermal stability of catalyst. In the last decades,

several functionalized polymers have been designed for immobilization of copper catalysts.[26-34] However, Copper ions in this type of catalysts can be easily oxidized to inactive Cu (II) or disproportionate to metallic copper. Also, in most cases polymer loaded copper catalysts showed higher activity only in hazardous organic solvents and reaction should be proceed in an inert atmosphere.

On the other hand, decreasing the amount of used copper catalysts in catalytic reactions is very important for industrial applications. Increasing the amount of used catalyst caused more pollution of catalyst and more solvent needs for reaction, separation process and recovery of catalyst. Therefore, developing an effective heterogeneous copper catalyst with high stability, low leaching, high loading and cleaner catalytic system is still demanded.

Herein, we describe the synthesis of copper loaded cross-linked ionic-imidazole polymer as a simple, inexpensive, and high loaded and efficient heterogeneous catalyst for use in the synthesis of 1,2,3-triazoles. Copper metalloenzymes are generated by complexation of imidazole of histidine amino acid in peptide structure and copper ion and these complextions are important in enzymatic reactions.[35,36] Therefore, investigation in catalytic activity of imidazole-copper polymer is one of the most interesting topics in polymer chemistry.

Experimental

Reagents and Analysis. $CuSO_4$, $NaBF_4$, $NaNO_3$, NaBr, NaOAc, N,N'-methylenebisacrylamide (MBA), 1-vinylimidazole (Vim) and 3-methacrylamido propyl trimethyl ammonium chloride (MAPTAC) were obtained from Aldrich. 1-Vinylimidazole was distilled before use and MAPTAC was extracted with diethyl ether. 2,2'-Azobisisobutyronitrile (AIBN, Kanto, 97%) was recrystallized from ethanol.

FT-IR spectra of samples were taken using an ABB Bomem MB-100 FTIR spectrophotometer. Thermogravimetric analysis (TGA) was acquired under a nitrogen atmosphere with a TGA Q 50 thermogravimetric analyzer. The morphology of the catalyst was observed using a Philips XL30 scanning electron microscope (SEM).

Synthesis of Catalyst. 1-Vinylimidazole (2 g), MAPTAC (4.5 g), MBA (0.5 g) and methanol (50 mL) were loaded into a 100 mL round bottom flask. The mixture was stirred and deoxygenated by argon for 20 min and then AIBN (0.1 g) was added to the mixture and the flask was equipped with a condenser and placed into an oil bath at 75 °C. After 15h, the solid products were filtered and washed three times with methanol and dried in vacuum at 50 °C and noted as cross-linked poly(imidazole-co-MAPTAC) (P[im/IL][Cl]).

The resulting powdered materials were subjected to anion exchange reaction. 0.3 g of powdered P[im/IL][Cl] was added to 50mL water and an excess amount of salt (10 fold than Cl anions in P[im/IL][Cl]) was added to the solution. The mixture was vigorously stirred (1000 rpm) for 3 days at room temperature. The solid products were then filtered, washed five times with water (5×100 mL) and twice with methanol (2×20 mL) and dried in vacuum at 50 °C.

0.5 g P[im/IL][Cl] was dispersed in 20 mL aqueous solution of $CuSO_4$ (Cu(II) mmol in solution was 0.5 fold of imidazole groups) by ultra-sonication for 25 min. Then the resulting mixture was stirred at 70 °C for 24 h. Afterward, the solid blue products were filtered and washed with water (5×50 mL) and dried at 50 °C to give P[imCu/IL][Cl]. The procedure for synthesis of other catalysts is the same as above method.

Determination of exchange of chloride ion with other ions. After exchange of chloride ions in P[im/IL][Cl] with other anions, the resulting catalysts were separated and the amount of released chloride anion was determined by titration with $AgNO_3$ based on standard Mohr's method. Bromide exchange was determined by ion chromatography. The results showed that the percentages of ion exchange process are 91, 83, 88 and 90% for P[im/IL][Br], P[im/IL][NO_3], P[im/IL][OAc] and P[im/IL][BF_4], respectively.

Determination of the copper content in catalysts. The catalyst (100 mg) was extracted with concentrated HCl (5 × 2 mL) in a screw-capped vessel, followed by treatment with concentrated nitric acid (2 mL) to digest the metal complex. The mixture was then transferred into a volumetric flask (100 mL), diluted 1:50 for the second time and was analyzed by the ICP analysis.

General procedure for the synthesis of 1,2,3-triazoles. Alkyne (0.5 mmol), alkyl halide (0.5 mmol), NaN_3 (0.6 mmol), sodium ascorbate (10 mg, 10 mol%) and P[imCu/IL][Cl] (5mg, 20mol%) were added to a 5-mL round bottom flask and 2 mL water was added and the mixture was stirred at 50 °C for appropriate time. After completion of the reaction (monitored by TLC) ethyl acetate was added to the flask and the catalyst was separated by filtration. The products were extracted with ethyl acetate/water mixture. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to give the corresponding 1,2,3-triazole. Obtained triazole was purified by recrystallization from EtOAc/hexane.

Results and discussion

The catalyst was synthesized by free radical polymerization of Vim and MAPTAC in the presence of MBA as cross-linker agent (Figure 1). Copolymerization was initiated by AIBN and the cross-linked insoluble copolymers were precipitated from the solution.[37-41] Afterward, P[im/IL][Cl] was subjected to ion exchange process to produce P[im/IL][Br], P[im/IL][NO$_3$], P[im/IL][OAc] and P[im/IL][BF$_4$]. The resulting powdered P[im/IL] with various anions were dispersed in CuSO$_4$ solution to produce copper loaded P[im/IL] (P[imCu/IL]). Imidazole groups in polymer backbone can strongly absorb copper ions. There are several reports that indicate imidazole/copper complexes improve the catalytic activity of copper ions.[32] The presence of ionic monomer MAPTAC in catalyst backbone can improve the substrate diffusion due to their ionic interaction with reactants.
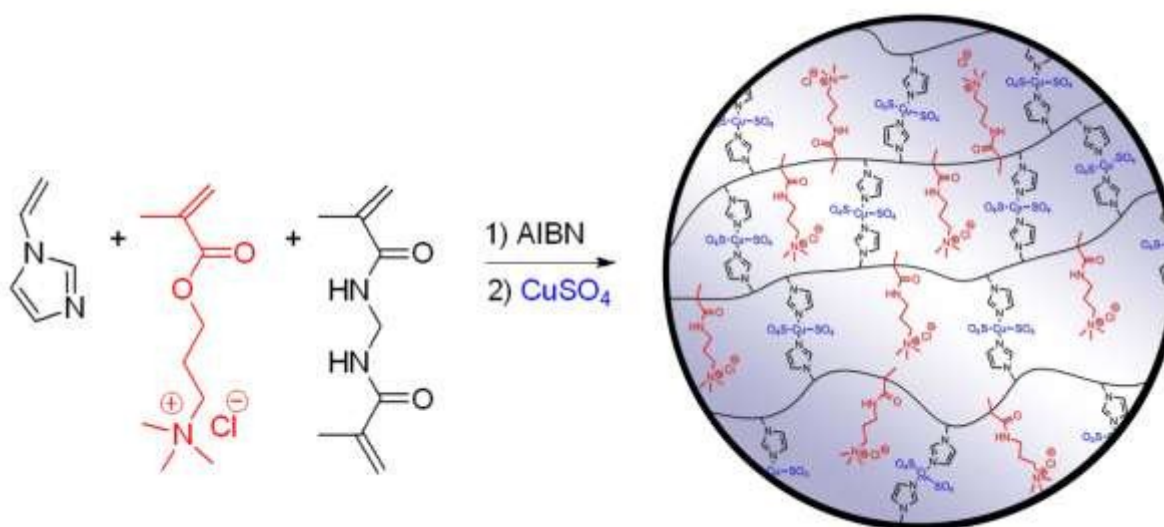
Figure 1. Synthesis of P[im/IL][Cl]

6

The FT-IR spectrum of P[im/IL][Cl] shows the stretching vibration bands at 1644, 1495, 1233 cm^{-1} which are attributed to carbonyl groups of MAPTAC and C=N, C=C and C-N of imidazole rings, respectively. The peak at 2927 cm^{-1} is attributed to C-H of alkyl chains (Figure 2). The FT-IR spectra of ion exchanged products are presented at supplementary data (Figure S1).

Similar pattern was observed in the FTIR spectrum of copper loaded catalyst (P[imCu/IL][Cl]) and a new peak also appeared at 1108 cm^{-1} which is attributed to SO$_4$ anions of CuSO$_4$ (Figure 2). The result confirms that CuSO$_4$ was successfully absorbed on the cross-linked copolymer.
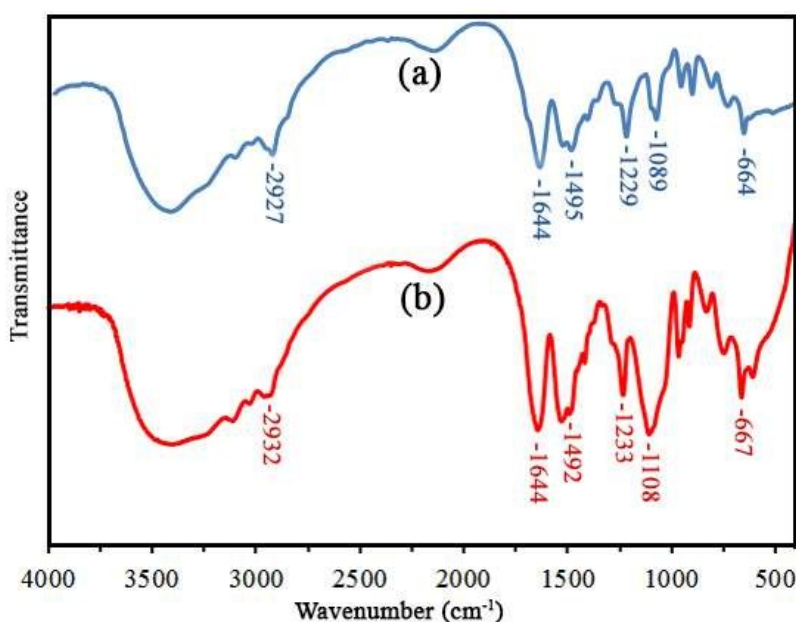
Figure 2. FT-IR spectra of P[im/IL][Cl] and P[imCu/IL][Cl]

Figure 3 shows the thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) of P[imCu/IL][Cl]. The weight loss at 150 °C was attributed to the loss of adsorbed water molecules in cross-linked polymer. The decomposition of catalyst started at 280 °C and it was

completely decomposed at 450 °C. This result demonstrates that catalyst is stable at range 25-280 °C which is absolutely suitable for various catalytic reactions. DTA curve shows three distinct peaks at 90, 320 and 450 °C which are attributed to adsorbed water molecules, MAPTAC and imidazole parts in polymer structure, respectively.
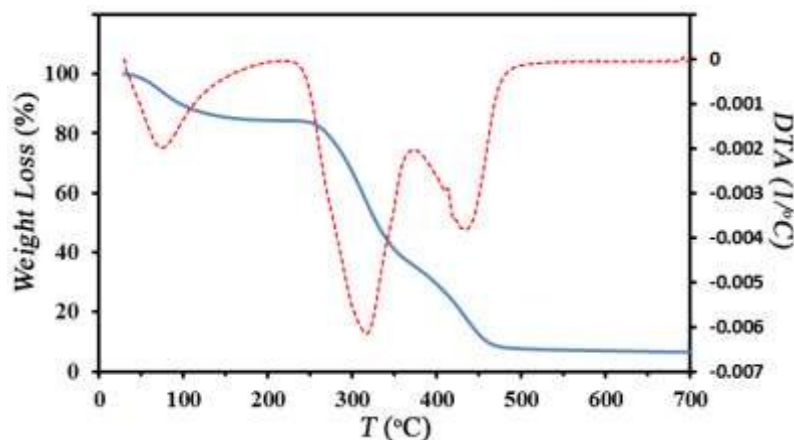
Figure 3. TGA and DTA curves of P[im/IL][Cl]

The SEM image of catalyst shows a rough surface for P[imCu/IL][Cl] (Figure 4). This surface morphology improves the catalyst activity due to the higher penetration of substrates onto the catalyst. EDX analysis also shows the presence of copper ion in catalyst structure (Figure 4).
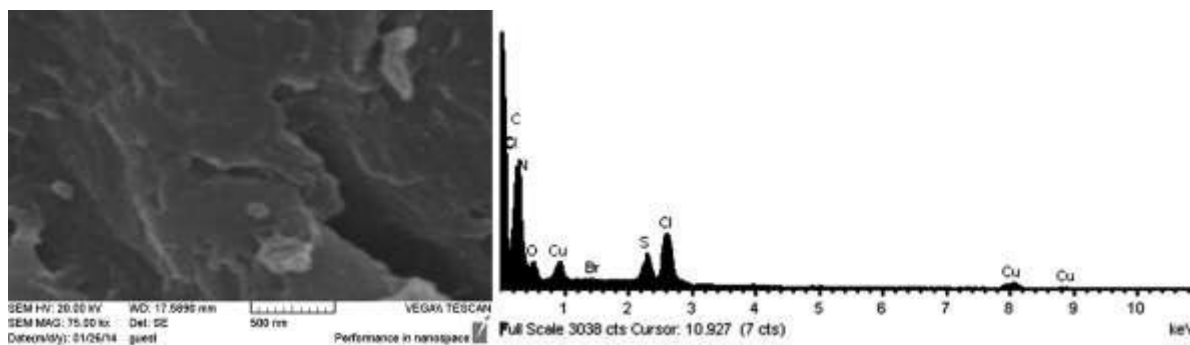
Figure 4. SEM image and EDX analysis of P[imCu/IL][Cl]

8

Atomic absorption and ICP-AES showed that the loading amount of copper ion in catalyst structure is about 1.3 mmol/g. The high loading level of immobilized copper ion resulted to using lower weight percent of catalyst in reaction. This feature of catalyst is especially useful when the catalyst is applied in large scale production.

Table 1 shows the control experiment and optimization of catalytic reaction by choosing reaction between phenyl acetylene benzyl bromide and sodium azide as model reaction. As seen in Table 1 without catalyst only a small amount of triazole product was obtained even by increasing reaction temperature to 70 °C. Moreover, P[im/IL][Cl] did not show any catalytic effect and less than 12% product was obtained at 100 °C in 8h. On the other hand, homogenous copper (II) sulfate increased the reaction yield up to 28% at 55 °C. Increasing the reaction temperature up to 110 °C gave 87% yield in 24h. But in this case mixtures of two regioisomers were obtained. In the next step catalytic performance of P[imCu/IL][Cl] was investigated and it was found that using 0.7 mol% of P[imCu/IL][Cl] increased the reaction yield to 99% in 2h at 55 °C. To investigate the effect of anion, various catalysts with different anions were examined and the results are presented in Table 1 entries 6-10. As a result, we observed that the order of catalytic activities of the five catalysts were; $Cl>OAc>Br>BF_4>NO_3$. This order of catalytic activity can be attributed to atomic radius of anions and chelation of copper ion by anions. Larger anions reduce substrates penetration onto the polymer network due to larger steric effect. Therefore, chloride counterion with smaller size gave better yield. On the other hand more basic anions like Cl and OAc can chelate copper ions better than less basic ones. Therefore, the transition state of reaction is more stable when P[imCu/IL][Cl] is used than P[imCu/IL][NO$_3$].

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Since first step of the reaction is nucleophilic substitution of sodium azide to benzyl bromide, basic anoins such as Cl and OAc can chelate Na^+ in NaN_3 and increase the reaction rate for first step and increase the yield of product.

Entry 11 shows that reducing the reaction temperature to room temperature reduced the yield of triazole product at the same reaction time. However, we found that in same condition longer time is required for completion of reaction (Entry 12). The optimization of catalyst loading in reaction shows that catalyst is highly active and even 0.1 mol% is enough for reaction and 99% yield is obtained at 55 °C. We decreased the catalyst amount to 0.0013 mol% (130 mol ppm) and surprisingly it was observed that reaction is completed with 91% yield and the turn over frequency of catalyst reached to 3889 h^{-1}. This result shows the high efficiency of P[imCu/IL][Cl] in Huisgen reaction.

Same reaction was performed in various solvents but 3/1 ratio of H_2O/t-BuOH shows the best result. It can be seen that the result of catalytic reaction in pure water (Entry 16) is as well as using mixture of solvents. This result provides a greener protocol for Huisgen reaction in water.

Entry 21 shows the effect of the presence of ionic monomer in the catalyst structure. It also can be seen that copper is adsorbed to poly(vinyl imidazole) less than ionic catalysts. Therefore, ionic monomer not only improves the catalytic performance but also increase copper adsorption and reduced the amount of used catalyst in the reaction.

To investigate the effect of imidazole groups as ligand we used the mixture of vinyl imidazole and copper sulfate in ratio of 2:1 as a homogenous catalyst. The result showed that imidazole groups increased the activity of copper by complexation (Entry 22). However, this catalyst is effective but it is a homogenous catalyst and its separation from the solution is an issue.

10

Table 1. Control experiment for synthesis of 1,3,5-triazole catalyzed by copper supported P[im/IL][Cl] [a]
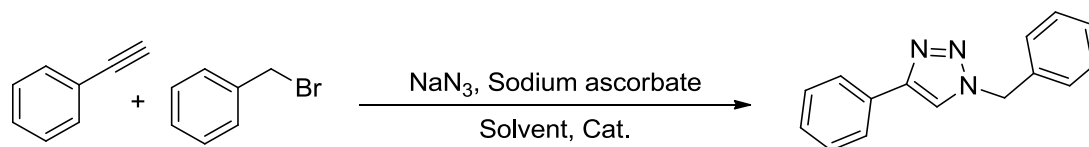
Entry	Catalyst	Cat. Loading (mol%)	Solvent	T (°C)	Time (h)	Yield (%)[b]	TOF (h^{-1})
1	-	-	H$_2$O/t-BuOH[c]	r.t	24	<1[d]	-
2	-	-	H$_2$O/t-BuOH	70	8	<3[d]	-
3	P[im/IL][Cl]	10mg	H$_2$O/t-BuOH	100	8	<12[d]	-
4	CuSO$_4$	5	H$_2$O/t-BuOH	55	10	28	0.6
5	CuSO$_4$	5	H$_2$O/t-BuOH	110	10	87[e]	2
6	P[imCu/IL][Cl]	0.7	H$_2$O/t-BuOH	55	2	99	71
7	P[imCu/IL][Br]	0.7	H$_2$O/t-BuOH	55	2	83	59
8	P[imCu/IL][NO$_3$]	0.7	H$_2$O/t-BuOH	55	2	72	51
9	P[imCu/IL][OAc]	0.7	H$_2$O/t-BuOH	55	2	88	63
10	P[imCu/IL][BF$_4$]	0.7	H$_2$O/t-BuOH	55	2	73	52
11	P[imCu/IL][Cl]	0.7	H$_2$O/t-BuOH	r.t.	2	80	57
12	P[imCu/IL][Cl]	0.7	H$_2$O/t-BuOH	r.t	9	99	16
13	P[imCu/IL][Cl]	0.4	H$_2$O/t-BuOH	55	2	99	124
14	P[imCu/IL][Cl]	0.1	H$_2$O/t-BuOH	55	2	99	495
15	P[imCu/IL][Cl]	0.0013	H$_2$O/t-BuOH	55	18	91[f]	3889
16	P[imCu/IL][Cl]	0.1	H$_2$O	55	2	91	455
17	P[imCu/IL][Cl]	0.1	t-BuOH	55	4	81	203
18	P[imCu/IL][Cl]	0.1	CH$_3$CN	55	4	83	208
19	P[imCu/IL][Cl]	0.1	CH$_3$OH	55	4	69	173
20	P[imCu/IL][Cl]	0.1	Toluene	55	4	37	93
21	P[imCu][g]	0.1	H$_2$O/t-BuOH	55	2	79	385
22	Vim/Cu[h]	0.1	H$_2$O/t-BuOH	55	2	99	495

[a] Reaction condition: phenyl acetylene (1 mmol), benzyl bromide (1 mmol), sodium azide (1.2 mmol), sodium ascorbate (10 mol%), solvent (3 mL).

[b] Isolated yield.

[c] The ratio of H$_2$O/t-BuOH is 3/1.

[d] Mainly recovery of the starting materials.

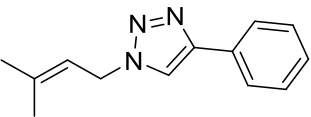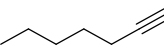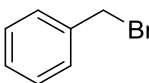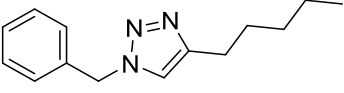[e] Mixture of regioisomers.
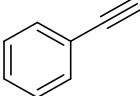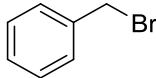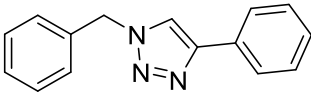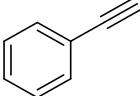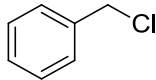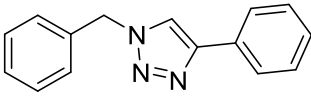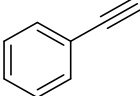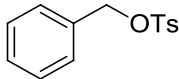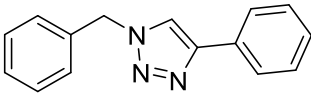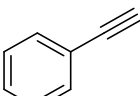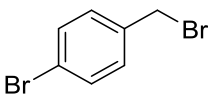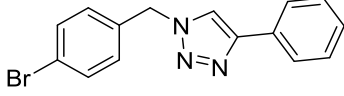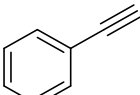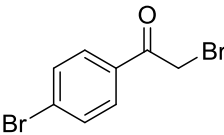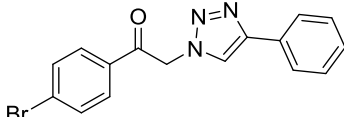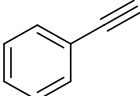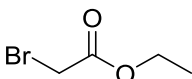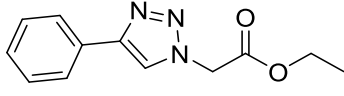
[f] 10 mmol scale of reaction.
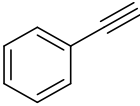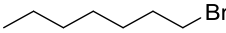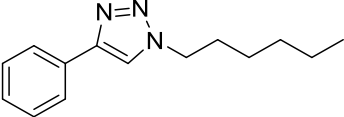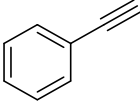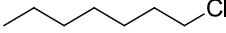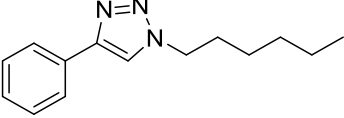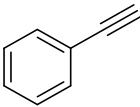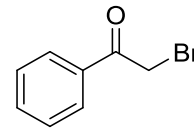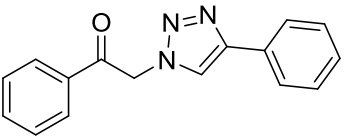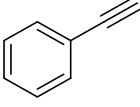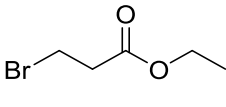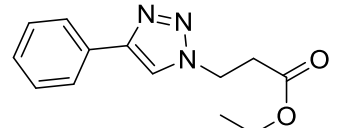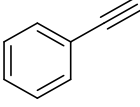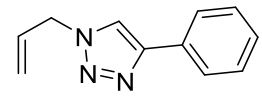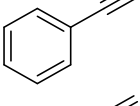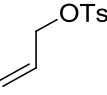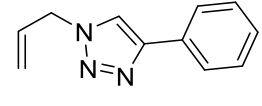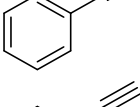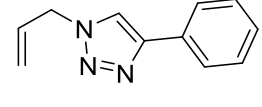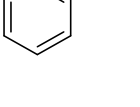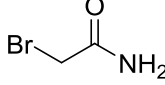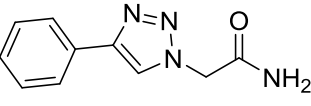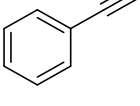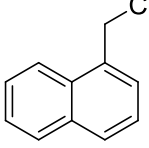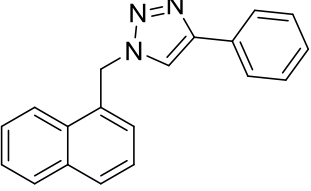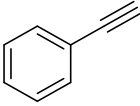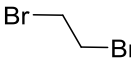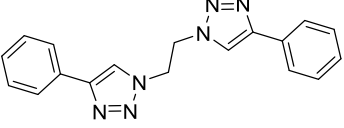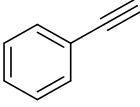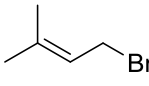
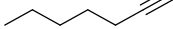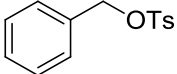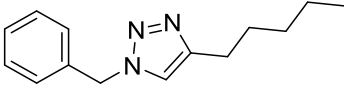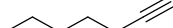[g] Cross-linked poly(vinyl imidazole) was used. Loading amount of copper on P[imCu] is 0.61 mmol/g.
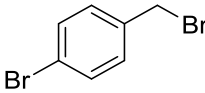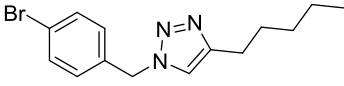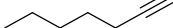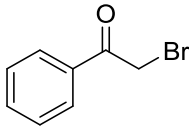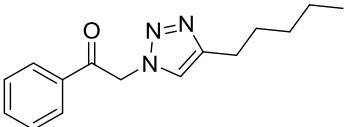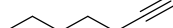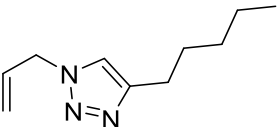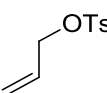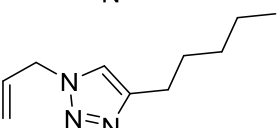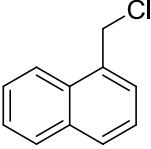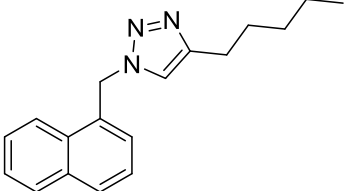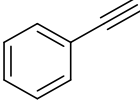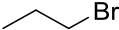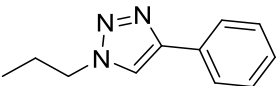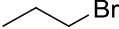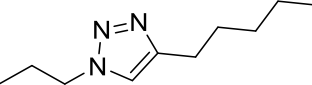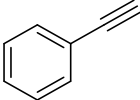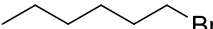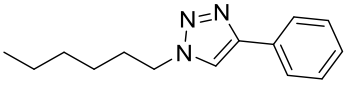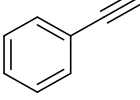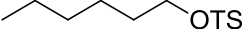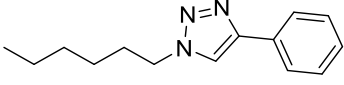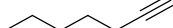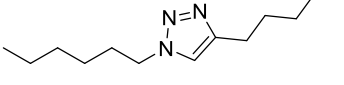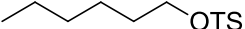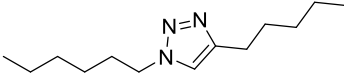
[h] Catalyst: mixture of vinyl imidazole (2 eq) and copper sulfate (1 eq).
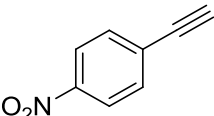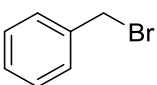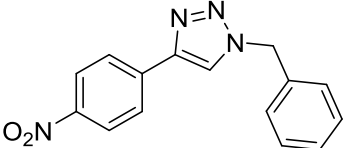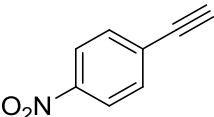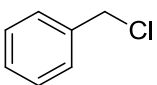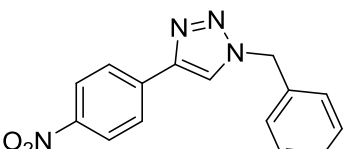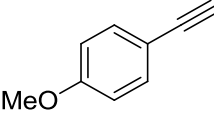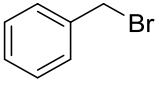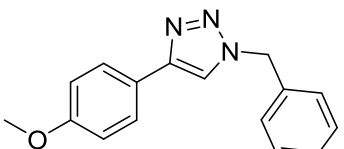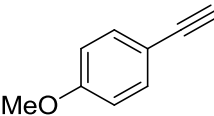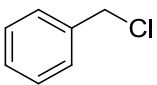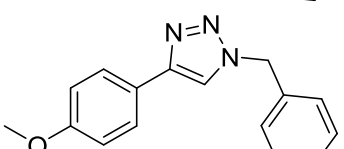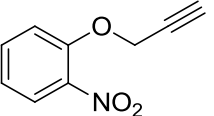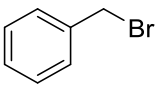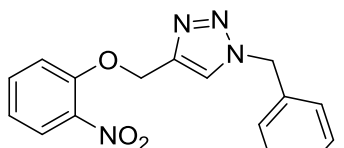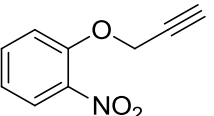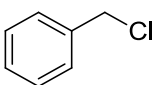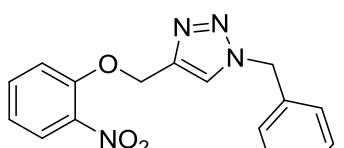
In continue, the scope of three-component reaction of alkyl halide, sodium azide and alkyne catalyzed by P[imCu/IL][Cl] was investigated on a number of assorted substrates in optimized condition (Table 2). Various substrates with electron withdrawing and electron donating groups reacted under optimized condition and gave corresponding triazoles in satisfactory yields. Compared to aryl substrates, reaction of alkyl substrates were slightly slower, although the yields of products were still excellent. These results show that P[imCu/IL][Cl] is a powerful catalyst for the synthesis of a broad range of triazoles.

Table 2. Huisgen 1,3-Dipolar Cycloaddition Catalyzed by P[imCu/IL][Cl][a]

Entry	Alkyne	Alkyl/Aryl halide	Product	Time (h)	Yield (%)[b]
1		Br		2	99
2		Cl		4	98
3		OTs		2	99
4				1.5	96
5				3.5	97
6				5	98

12

7			4	96
8			8	94
9			3.5	98
10			3	93
11			3	94
12			2	97
13			4	93
14			5	98
15			6	90
16			5	89
17			2	90
18			4	96

19			3	95
20			4	95
21			6	96
22			3	94
23			3	95
24			6	90
25			2	92
26			4	90
27			3	95
28			3	95
29			4	92
30			3	93

31	O₂N–C₆H₄–C≡CH	benzyl Br	triazole product (O₂N)	2	95
32	O₂N–C₆H₄–C≡CH	benzyl Cl	triazole product (O₂N)	3	95
33	MeO–C₆H₄–C≡CH	benzyl Br	triazole product (MeO)	3	91
34	MeO–C₆H₄–C≡CH	benzyl Cl	triazole product (MeO)	3	86
35	2-NO₂-C₆H₄–O–CH₂–C≡CH	benzyl Br	triazole product (NO₂)	4	90
36	2-NO₂-C₆H₄–O–CH₂–C≡CH	benzyl Cl	triazole product (NO₂)	4	85

[a] Reaction condition: alkyne (0.5 mmol), alkyl halide (0.5 mmol), NaN₃ (1 mmol), sodium ascorbate (10 mol%), P[imCu/IL][Cl] (0.1 mol%), solvent (H₂O/*t*-BuOH, 3/1), 55 °C.
[b] Isolated yield.

Along with the high activity of P[imCu/IL][Cl] in a low weight percent, another useful advantage of the catalyst is its reusability. At the end of a reaction, the catalyst was easily separated from solution by simple filtration. The reusability of P[imCu/IL][Cl] was investigated in three component reaction between phenyl acetylene, benzyl bromide and sodium azide as model reaction (Table 2, entry 1). In order to prevent catalyst mass losing, at the end of each

cycle the catalyst was separated by centrifuge, washed and dried for next runs. As shown in Figure 5 the catalyst was reused 12 times and no significant loss of activity was observed.
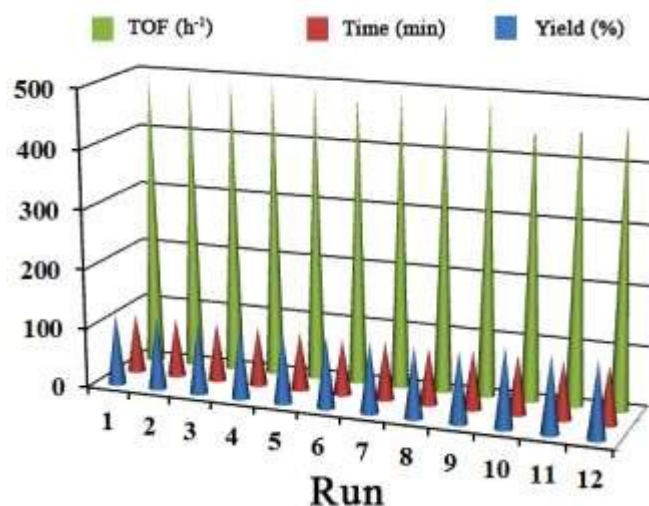
Figure 5. Recycling experiment.

In order to investigate catalyst leaching, reaction between phenyl acetylene, benzyl bromide, NaN_3 was chosen as model reaction. The reaction was performed in optimized condition and after half of the reaction time (60 min) the catalyst was separated from the solution by hot filtration using hot ethyl acetate. The rest of reaction mixture (in the absence of catalyst) was allowed to stir for another 60 min. As seen in Figure 6 no triazole was produced after catalyst removal. Moreover, atomic absorption analysis of triazole product shows no copper ion in it. These results show that catalyst is truly heterogeneous and catalyst leaching is negligible under reaction condition.
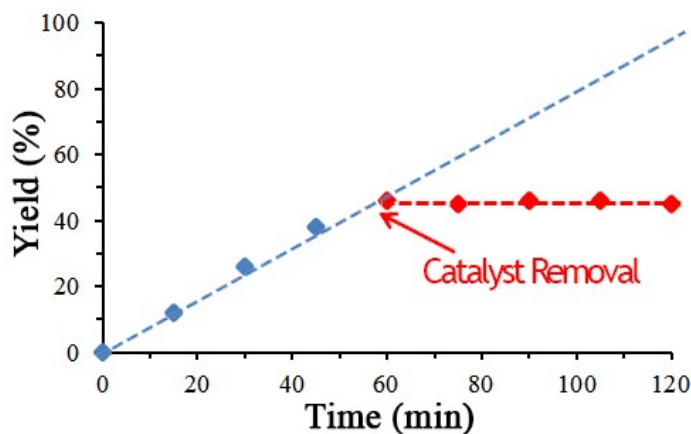
Figure 6. Leaching experiment.

Conclusion

In conclusion, we have prepared a novel heterogeneous copper loaded catalyst based on cross-linked poly(ionic liquid)s. The resulted catalyst was proven to be an effective and robust catalyst for preparation of 1,2,3-triazoles in a green way. The catalyst was easily prepared in large scale amount with high loading level of copper ion. The catalyst was recovered and reused several times without significant loss of activity. Because of high activity of catalyst in ppm amount the present protocol and catalyst can be used in large scale industrial applications.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

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