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Eco-Efficient, Green, and Scalable Synthesis of 1,2,3-Triazoles Catalyzed by Cu(I) Catalyst on Waste Oyster Shell Powders

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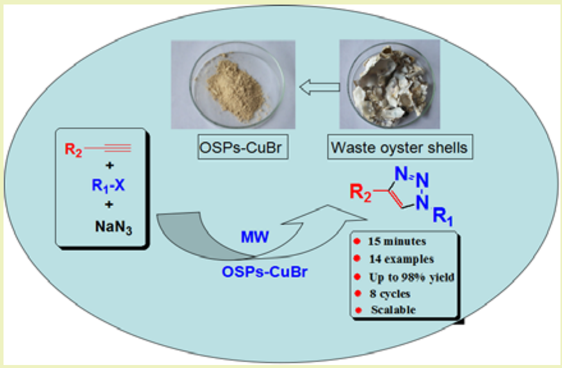
Supporting Information

ABSTRACT: An efficient and recyclable waste oyster shell powders (OSPs)-supported CuBr catalyst (OSPs−CuBr) has been successfully prepared and well characterized by Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA), atomic absorption spectroscopy (AAS), and powder X-ray diffraction (XRD). Then, OSPs−CuBr was used as a heterogeneous catalyst for the one-pot multicomponent synthesis of 1,4-disubstituted 1,2,3-triazole derivatives via a Cu(I)-catalyzed azide−alkyne 1,3-dipolar cycloaddition (CuAAC) reaction. Compared with a $CaCO_3$−CuBr catalyst, the OSPs−CuBr catalyst showed higher catalytic activity and stability characteristics. The chitin and protein molecules on the OSP particles surfaces play an important role in the chelation of the CuBr species, which leads to the better chemical stability of OSPs−CuBr. The 1,2,3-triazoles are readily obtained in good to excellent yields and on a multigram scale by the reaction of aryl/alkyl halides, alkynes, and NaN_3 under microwave irradiation conditions. It also showed good reusability, could be easily recovered through filtration and washing, and was reused at least eight times with virtually no evident loss of catalytic performance.



KEYWORDS: *Oyster shell powders, Heterogeneous catalyst, 1,2,3-Triazoles, Click chemistry, CuAAC, Green chemistry*

INTRODUCTION

Among the various five-membered heterocyclic compounds, 1,2,3-triazole derivatives are very important pharmacophores whose subunits are often found as a key nucleus of biologically active molecules.[1] In addition, triazole-containing structures have attracted attention for their coordination properties,[2] and some related complexes have displayed efficient antitumor activities.[3] So synthesis of 1,2,3-triazoles is one of the important topics in the preparation of heterocyclic compounds. Therefore, considerable efforts have been made in the development of efficient strategies for their preparation.

Up to now, the most efficient, convenient, and reliable method for the construction of the 1,4-disubstituted 1,2,3-triazole framework is the one-pot multicomponent copper-catalyzed azide−alkyne cycloaddition (CuAAC) reaction under microwave or ultrasound irradiation.[4−9]

In general, homogeneous copper(I) catalysts have been used to catalyze one-pot multicomponent synthesis of 1,2,3-triazoles from benzyl/alkyl halides, alkynes, and NaN_3.[4,5] Although homogeneous copper(I) catalysts have gained enormous relevance, industrial applications of these reactions remain challenging because the homogeneous catalysts require the use of ligands, and the preparation of them involves the use of toxic and volatile organic solvents that are often not easy to handle. Furthermore, the copper metal contamination in the final products is a major concern for the homogeneous catalytic system because it is frequently reached at an unacceptable level. These drawbacks counteract their applications.

In order to overcome these drawbacks, several research groups have made enormous efforts to develop heterogeneous protocols for the synthesis of 1,2,3-triazoles via a CuAAC reaction. So far, many efforts have been made to overcome these problems through immobilization of metal nanoparticles on solid supports, such as charcoal,[10] magnetic nanoparticles (MNPs),[9,11−13] silica,[14] polymers,[15−19] and zeolite.[20] However, common problems encountered while using these heterogeneous catalysts are higher cost and the requirement for tedious and time-consuming procedures for catalyst preparation.

One possible way to reduce the costs of the catalysts is to use agricultural wastes as support materials of the catalysts. The use of waste materials as supports of the catalysts (instead of discarding) also reduces the cost of waste handling and disposal. Recently, there has been increasing interest in this area.[21]

Oyster (*Crassostrea gigas*) abounds in Xiamen (coastal city of southeast China), and it is one of the most popular seafoods in that city. Although millions of tons of oyster shells are generated there every year, most of the oyster shells are abandoned without any pretreatment. Therefore, disposal of

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waste oyster shells in Xiamen is inevitably associated with environmental problems, as the degradation of oyster shells at ambient temperature is slow and produces noxious odors that seriously affect the quality of life and the living environment of nearby residents.

In recent years, ground OSPs have been successfully reused as various construction materials and as promising adsorbents of metal ions in sewage and so on.[22−25]

Unfortunately, as far as we know, their potential utilization as supports of heterogeneous catalysts is less explored. So far, only one paper has reported successful use of oyster shell wastes as catalyst support for the transesterification of soybean oil.[26]

As part of our continuing interest in the further improvement the practicability and eco-friendliness of the CuAAC reaction, we report herein a simple, green, and scale-up process for one-pot multicomponent synthesis of 1,2,3-triazoles from aryl/alkyl halides, alkynes, and NaN_3 in water, which are catalyzed by a heterogeneous copper(I) catalyst, OSPs−CuBr, via combination of a one-pot multicomponent CuAAC reaction and microwave irradiation. The catalyst could be easily recovered from the reaction mixture by a simple filtration and reused at least eight times without significant loss of its catalytic activity. To the best of our knowledge, no examples of the one-pot and scale-up synthesis of 1,2,3-triazole derivatives by a waste material-supported CuBr catalyst have been reported.

EXPERIMENTAL SECTION

General. Discarded oyster shells were collected from an oyster farm in Tong'an district, Xiamen. All reagents and solvents were obtained from commercial sources and used without further purification. All the one-pot CuAAC reactions were carried out in a professional microwave reactor equipped with a stirring bar. The utilized microwave benchtop reactor (MAS-II) is manufactured by Sineo Microwave Chemistry Technology (Shanghai) Co. The IR spectra were obtained using a FTIR (4000−400 cm^{-1}) spectrometer (Nicolet Nexus FTIR spectrometer, U.S.A.) at 4 cm^{-1} resolution and 32 scans. Samples were prepared using the KBr disc method. The OSPs−CuBr catalyst was determined by atomic absorption spectrophotometry (AAS) using standard methods with a Varian AA275 atomic absorption spectrophotometer (U.S.A.). XRD was used to characterize the crystalline structure of OSPs−CuBr on a Bruker D8 Advance (Germany) using Cu $K\alpha$ radiation. NMR spectra were acquired in $CDCl_3$ on a Bruker DMX-400 spectrometer at 400 MHz for ^1H NMR; the chemical shifts are given in δ values from TMS as an internal standard.

Preparation of the OSPs- and $CaCO_3$-Supported CuBr Catalysts. A total of 0.5 g of CuBr was added into 5.0 g of OSPs in 50.0 mL of deionized water under the protection of a nitrogen atmosphere. The resulting mixture was allowed to stir at room temperature until the solution turned from orange to colorless. The collected powders were then washed with ethanol followed by drying under vacuum at 50 °C overnight for further use. Calcium carbonate-supported copper catalyst ($CaCO_3$−CuBr) was prepared by the same procedure.

Synthesis of 1,2,3-Triazoles Catalyzed by OSPs−CuBr and $CaCO_3$−CuBr Catalysts. Three substrates, primary halide (1.5 mmol), NaN_3 (1.5 mmol), and terminal alkyne (1.5 mmol), were combined, followed by adding a copper(I) catalyst (2.5 mol %) in H_2O (5.0 mL) in a 10 mL round-bottomed flask. The mixture was heated and stirred at 70 °C under microwave irradiation (480 W) for 15 min. Then the reaction mixture was cooled to room temperature, and the copper(I) catalyst was isolated by simple filtration. Then, the residual mixture was extracted three times with ethyl acetate (3 × 20 mL). The combined organic layer was washed with saturated brine and then dried with anhydrous $MgSO_4$. Ethyl acetate was removed by rotary evaporation. The crude product was purified by flash chromatography on silica gel to give the desired 1,2,3-triazoles.

Recycling and Reuse of OSPs−CuBr and $CaCO_3$−CuBr Catalysts. After completion of the CuAAC reaction, the OSPs−CuBr or $CaCO_3$−CuBr catalyst was isolated by simple filtration from the reaction system and washed with water and ethanol. After drying under vacuum at 50 °C for 2 h, the recovered catalyst was used for the next cycle under the same conditions. The catalyst could be recycled and reused at least eight times with a negligible drop in its catalytic activity.

RESULTS AND DISCUSSION

Disposal of oyster shell wastes in Xiamen is inevitably associated with environmental problems. Most of the oyster shell wastes are abandoned without any pretreatment (Figure 1A).

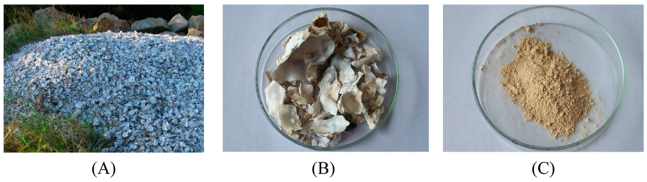


Figure 1. (A) Enormous amount of oyster shell wastes disposed at coastal areas. (B) Oyster shells rinsed thoroughly by ultrasonic cleaner. (C) OSPs−CuBr catalyst prepared from oyster shell wastes.

Sands and seaweeds were removed from raw oyster shells with deionized water using ultrasonic irradiation until the water was clear (Figure 1B). After being dried, the oyster shells were roughly crushed using a hammer, ground into powders with a pestle and mortar, and then screened over 100 mesh sieve. The powdered shell was dried, and then waste oyster shell-supported CuBr catalyst (OSPs−CuBr) was prepared by treating OSPs with CuBr (Figure 1C).

OSPs−CuBr and $CaCO_3$−CuBr have been characterized by FTIR, TGA, AAS, and XRD. Table 1 shows the FTIR spectra of OSPs and $CaCO_3$ before and after the complexing with CuBr. As shown in Table 1, the $-CO_3^{2-}$ stretching peak of OSPs appearing at 1418 cm^{-1} was shifted to 1425 cm^{-1} after complexing with CuBr. Furthermore, the $-CO_3^{2-}$ bending vibration absorption peaks at 877 and 712 cm^{-1} were shifted to lower wavenumbers 875 and 710 cm^{-1}, respectively. This is probably caused by the coordination effect of copper(I) with the surface chitin and protein molecules of the OSPs. In contrast, when $CaCO_3$ is complexed with CuBr, the $-CO_3^{2-}$ stretching peak appearing at 1425 cm^{-1} was shifted to lower wavenumber 1421 cm^{-1}. The lowering in frequency of the above peak indicates the physical adsorption of CuBr by $CaCO_3$. However, the $-CO_3^{2-}$ bending vibration absorption peaks at 878 and 712 cm^{-1} have no observable peak shift on the characteristic IR absorption peaks before and after the adsorption with CuBr as shown in Table 1.

The percentages of copper contents of the fresh OSPs−CuBr and the recycled OSPs−CuBr after eight consecutive trials were determined by AAS (Table 1). The catalysts were stirred in diluted HNO_3 for 10 h and then subjected to AAS analysis. The copper(I) content of the catalyst OSPs−CuBr after eight cycles was found to be 3.251% detected by AAS, which was slightly lower than the catalyst 1 (3.648 wt %). In contrast, the percentage of copper contents of $CaCO_3$−CuBr and the reused $CaCO_3$−CuBr after eight cycles were found to be 3.863 and 0.418 wt %, respectively. An obvious conclusion can be drawn that the chitin and protein molecules on OSP particles surface play important roles in the chelation of the CuBr species. Thus, the CuAAC reaction catalyzed by OSPs−CuBr makes the

Table 1. FTIR and Microanalysis of OSPs−CuBr and $CaCO_3$−CuBr Catalysts

sample	FTIR (KBr, cm^{-1})			microanalysis (wt %)	
	ν_1-CO_3^{2-}	ν_2-CO_3^{2-}	ν_3-CO_3^{2-}	Cu[a]	Cu[b]
OSPs	1418	877	712	–	–
OSPs−CuBr	1425	875	710	3.648	3.251
$CaCO_3$	1425	878	712	–	–
$CaCO_3$−CuBr	1421	877	712	3.863	0.418

[a] AAS analysis results of fresh catalysts. [b] AAS analysis results of OSPs−CuBr and $CaCO_3$−CuBr after eight consecutive trials.

synthesis process of 1,2,3-triazoles more practical and cost effective.

The thermal behaviors of OSPs−CuBr and $CaCO_3$−CuBr are further investigated by TGA. As shown in Figure 2, a slow weight loss at 100 °C (about 0.5 wt.%) was observed, which could be assigned to the loss of the absorbed water from the surface of the samples. The TGA curve of OSPs−CuBr reveals a weight loss (8.02 wt %) from 100 to 600 °C, resulting from the decomposition of chitin and protein molecules in the oyster shell powders. A sharp drop in the weight of OSPs−CuBr at 600−730 °C indicated a phase change from $CaCO_3$ to CaO (Figure 1b), and complete thermal decomposition was achieved at 730 °C as the TGA curve became parallel to the *X*-axis, indicating that most of the $CaCO_3$ was converted to CaO. Obviously, $CaCO_3$−CuBr exhibits a higher thermal stability rather than OSPs−CuBr. No obvious weight loss is observed under 600 °C, and a sharp decrease in the weight of $CaCO_3$−CuBr at 600−745 °C indicated a phase change from to CaO (Figure 1a), which can be assigned to the decomposition of $CaCO_3$. The OSPs−CuBr and $CaCO_3$−CuBr catalysts possess good thermal stabilities (up to 200 °C), which meet the demands for potential applications in catalysis.

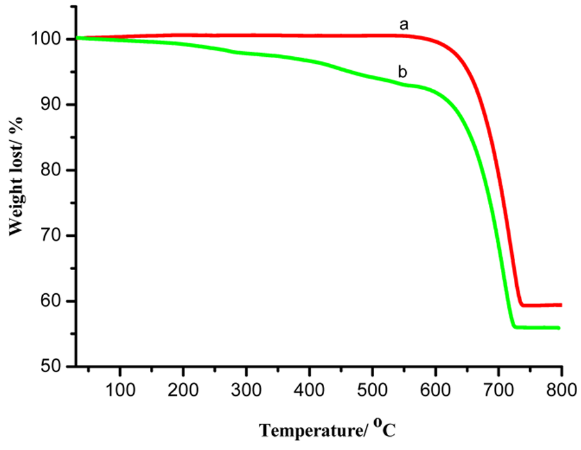


Figure 2. TG curves of (a) $CaCO_3$−CuBr and (b) OSPs−CuBr.

The XRD patterns of OSPs, OSPs−CuBr, and $CaCO_3$−CuBr are presented in Figure 3. The obtained XRD patterns of the OSPs−CuBr and $CaCO_3$−CuBr crystals display the following diffraction peaks (2θ[deg]): 23.30, 29.64, 36.21, 39.73, 43.42, 47.70, and 48.71, which can be correlated to the hkl indices (012), (104), (110), (113), (202), (024), and (116), respectively, of calcite (JCPDS card number: 72-1652). As shown in Figure 3, no additional diffraction peaks of CuBr in XRD patterns of OSPs−CuBr and $CaCO_3$−CuBr were observed in the XRD patterns of these catalysts, suggesting that amorphous CuBr species highly dispersed onto OSPs and $CaCO_3$ supporter surface.

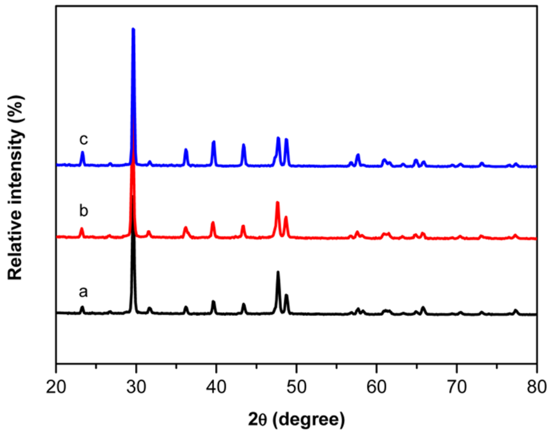
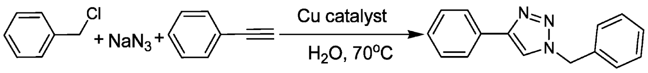


Figure 3. XRD pictures: (a) OSPs, (b) OSPs−CuBr, and (c) $CaCO_3$−CuBr.

Effect of Copper Source on One-Pot Synthesis of 1,2,3-Triazoles. Initially, the reaction between benzyl chloride, NaN_3, and phenylacetylene was chosen as a model reaction to investigate the optimization of the reaction conditions. The reaction was performed by conventional heating or preferably under microwave (MW) irradiation in order to reduce the reaction time. The results are summarized in Table 2.

Table 2. Effect of Copper Source on One-Pot Synthesis of 1-Benzyl-4-phenyl-1*H*-1,2,3-triazole under Microwave-Assisted and Conventional Heating Conditions[a]

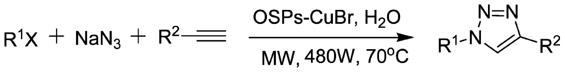


entry	catalyst	time[c]/time[c] (min)	yield[d]/yield[d] (%)
1	$Cu(OAc)_2$	15/240	12/73
2	$CuSO_4{\cdot}5H_2O$	15/240	36/52
3	Cu_2O	15/240	67/51
4	CuCl	15/240	75/69
5	CuBr	15/240	82/78
6	$CaCO_3$−CuBr	15/240	91/89
7	OSPs−$CuSO_4$[b]	15/240	41/69
8	OSPs−CuBr	15/240/15[c]	96/91/19[d]

[a] 1.5 mmol of benzyl chloride, 1.5 mmol of NaN_3, 1.5 mmol of phenylacetylene, 2.5 mol % of catalyst, and H_2O 5.0 mL. [b] OSPs-supported $CuSO_4{\cdot}5H_2O$ catalyst was prepared by the same procedure as OSP−CuBr or $CaCO_3$−CuBr. [c] Reaction time under conventional heating and microwave irradiation conditions, respectively. [d] Isolated yield of 1,2,3-triazole under conventional heating and microwave irradiation conditions, respectively.

Optimization studies revealed that when the reaction was carried out using copper(II) catalysts, such as $Cu(OAc)_2$, $CuSO_4{\cdot}5H_2O$, and OSPs−$CuSO_4$ for 15 min at 70 °C under MW irradiation conditions, 1-benzyl-4-phenyl-1*H*-1,2,3-triazole

Table 3. One-Pot Synthesis of 1,2,3-Triazoles



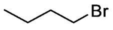
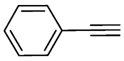
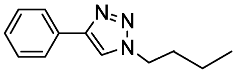
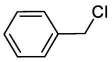
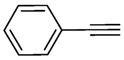
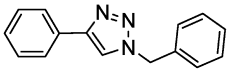
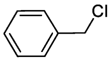
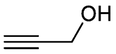
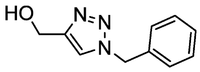
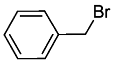
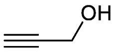
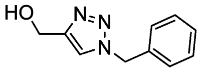
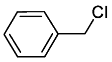
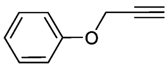
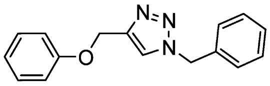
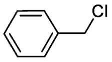
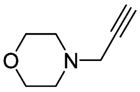
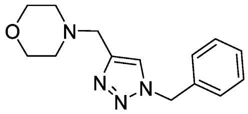
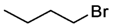
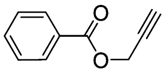
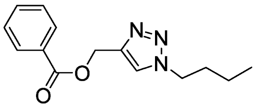
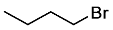
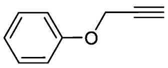
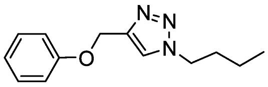
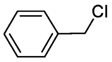
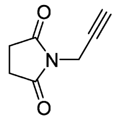
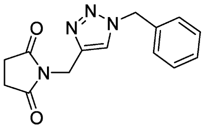
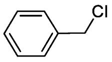
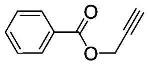
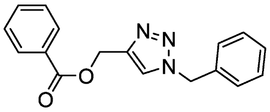
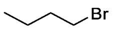
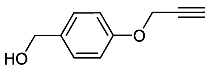
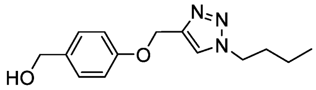
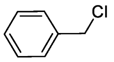
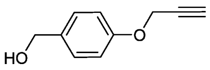
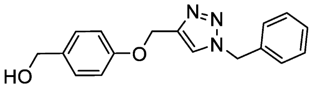
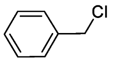
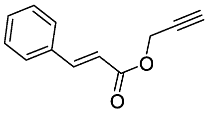
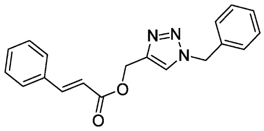
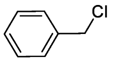
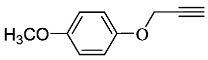
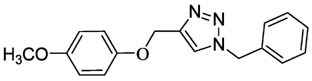
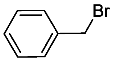
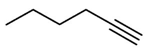
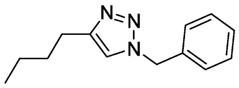
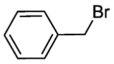
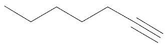
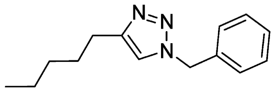
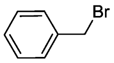
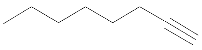
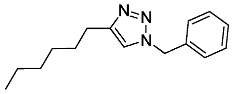
Entry	Halide	Alkyne	Product	Time [b]	Yield [c]
1				15 min	95%
2				15 min	98%
3				15 min	94%
4				15 min	96%
5				15 min	94%
6				15 min	92%
7				15 min	91%
8				15 min	94%
9				15 min	91%
10				15 min	93%
11				15 min	92%
12				15 min	94%
13				15 min	91%

Table 3. continued

Entry	Halide	Alkyne	Product	Time [b]	Yield [c]
14				15 min	94%
15				15 min	87%
16				15 min	87%
17				15 min	83%

[a] 1.5 mmol of alkyl halides, 1.5 mmol of NaN_3, 1.5 mmol of alkyne, 2.5 mol % of catalyst, and H_2O 5.0 mL. [b] Overall time, including heating time and incubating time. [c] Isolated yields.

could be obtained in 12%, 36%, and 41% isolated yield, respectively (Table 2, entries 1, 2, and 7, respectively).

Next, various other copper salt catalysts were screened in the one-pot synthesis 1,2,3-triazoles of phenylacetylene in water (Table 2, entries 3−5, 6, and 8, respectively). When the reaction was carried out using Cu_2O, CuCl, or CuBr as the catalyst, the product could be obtained in moderate to good yield of 67%, 75%, and 82%, respectively (Table 2, entries 3, 4, and 5, respectively). To our delight, after screening experiments with the other supported catalysts, such as $CaCO_3$−CuBr and OSPs−CuBr, the reaction performed smoothly with the use of them compared to any other copper sources (Table 2, entries 6 and 8, respectively). Furthermore, OSPs−CuBr was identified as the most effective catalyst for this reaction and yielded the product in 96% isolated yield (Table 2, entry 8). The catalytic activity of OSPs−CuBr is better than $CaCO_3$−CuBr, possibly because the Cu(I) species chelated by chitin and protein molecules in the OSP supporter resulted in more stable Cu(I) than was physically absorbed on the $CaCO_3$ supporter.

Under conventional heating conditions, we investigated the activity of the catalysts with respect to time for the formation of triazole at 70 °C. After 240 min, when the supported CuBr, such as $CaCO_3$−CuBr or OSPs−CuBr, was used as the catalyst, the yields of the obtained 1,2,3-triazole were found to be 89% and 91%, respectively (Table 2). In addition, when OSPs−CuBr was used as the catalyst, the reaction has only a 19% yield after 15 min under conventional heating conditions. Compared with the traditional heating method, the use of microwave irradiation could dramatically reduce the reaction time.

Encouraged by these results, the OSPs−CuBr catalyst was reasonably chosen as the best heterogeneous Cu(I) catalyst for the one-pot CuAAC reaction under microwave irradiation conditions due to its high efficiency, stability, and recyclability.

From a practical point of view, heterogeneous copper(I) catalysts must accept a wide variety of substrates as large as possible, which contain different structures and functional groups. Thus, with the optimal conditions in hand, the substrate scope of the copper(I)-catalyzed one-pot CuAAC reaction between different alkynes and various aliphatic or aromatic halides was explored with OSPs−CuBr, which has been proven to be the most effective catalyst (Table 2, entry 8). The results are summarized in Table 3.

It was found that all the reactions proceeded smoothly to give the corresponding 1,4-disubstituted-1,2,3-triazoles in high yields, which clearly indicated the generality and scope of the reaction with respect to various terminal alkynes and halides.

In general, no significant difference in reactivity was observed for the examined reactants with varied electronic properties. Both electron-rich and electron-poor alkynes as reactants generated good to excellent yields of the products. The reactivity of 4-bromobutane was found to be less reactive than that of benzyl halides, and primary bromides displayed higher activities than their chloride analogues. Functional groups like −OH, −O−, and −COOR were highly tolerated, which did not break down under one-pot CuAAC reaction conditions. Under the optimal condition, the nonactivated alkyl-substituted alkynes, such as 1-pentyne, 1-hexyne, or 1-octyne, can react smoothly with benzyl bromide/NaN_3 and give good yields (entries 15−17, 83−87%). In addition, the reaction was also carried out using bromobenzene as the halide, but unfortunately, very low conversion was observed on TLC.

Reuse Test of OSPs−CuBr and $CaCO_3$−CuBr Catalysts. To achieve both economic and environmental benefits, a heterogeneous catalyst should be stable enough to tolerate several iterative reactions, and its high activity and facile recovery are also extremely desirable, especially if the reactions are performed on a large scale.

In order to make our catalytic system greener and economical, we focused on the reusability of OSPs−CuBr and $CaCO_3$−CuBr catalysts on multicomponent reaction of phenyl acetylene, NaN_3, and benzyl chloride. To this point, a series of consecutive reactions were carried out under the same conditions using the reused OSPs−CuBr and $CaCO_3$−CuBr catalysts. The results are shown in Figure 4. The obtained results indicated no noticeable drop in the product yields or the catalytic activity of the OSPs-supported catalyst even after eight cycles, suggesting that CuBr leaching is not significant for the

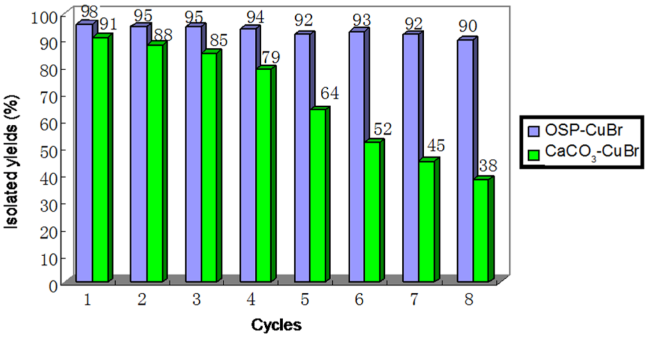


Figure 4. Reusability of the catalysts OSPs−CuBr and $CaCO_3$−CuBr using NaN_3, benzyl chloride, and phenylacetylene as starting materials under microwave irradiation in water.

Table 4. Large-Scale Synthesis of 1-Benzyl-4-Phenyl-1*H*-1,2,3-Triazole

entry	scale (mmol)	H_2O (mL)	yield (%)[a]
1	1.5	5	96
2	30	50	94
3[b]	30	50	90
4[c]	30	50	88
5[d]	30	50	81
6	60	100	90
7	120	140	87

[a] Isolated yield. [b] Catalyst recycled from entry 2 and used for second run. [c] Third run. [d] Fourth run.

heterogeneous OSPs−CuBr catalyst. However, the reactions catalyzed by the $CaCO_3$−CuBr catalyst witnessed an increasingly low yield. The results showed that the yield decreased after several reused cycles (only 38% after eight cycles). The copper(I) content of the catalyst OSPs−CuBr after eight cycles was found to be 3.251 wt % detected by AAS, which was slightly lower than the fresh catalyst OSPs−CuBr (3.648 wt %). However, AAS analysis shown the copper(I) content of $CaCO_3$-supported catalyst obviously decreased from 3.863 to 0.418 wt % after eight cycles.

The obvious differences of catalytic ability after eight cycles between OSPs−CuBr and $CaCO_3$−CuBr catalysts could be explained by the chitin and protein molecules on the OSP particles surfaces, which play important roles in the chelation of CuBr. Thus, this makes the OSPs−CuBr catalyst more preferable.

Large-Scale Synthesis of 1-Benzyl-4-phenyl-1*H*-1,2,3-triazole. In order to evaluate the feasibility of applying this method in a preparative scale, a large-scale experiment for the synthesis of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole was carried out in the presence of benzyl chloride, NaN_3, and phenylacetylene in water under the above optimum reaction conditions. The reactions were found to proceed successfully, and the corresponding product was obtained in good yields. When the scale of the reaction was 30 mmol, the catalyst could be recycled and reused at least four times and still maintained good yield. Importantly, when the scale of the reaction was 120 mmol, the yield of purified 1-benzyl-4-phenyl-1*H*-1,2,3-triazole was up to 87%. The detailed results are summarized in Table 4. Comparing with the other methods, this process realizes clean and efficient synthesis of 1,2,3-triazoles and provides good yields for them under mild conditions, which is especially important for practical applications in industry.

■ CONCLUSIONS

In conclusion, a facile, recyclable, heterogeneous copper(I) catalyst using biowaste OSPs as support was developed for the first time for a one-pot CuAAC reaction under microwave irradiation in water. The low-leaching and ligand-free properties allow it to have higher yields than that of $CaCO_3$−CuBr. The striking catalytic efficiency and stability of the OSPs−CuBr catalyst has been attributed to the chelation of the copper(I) species with the surface chitin and protein molecules of the OSPs. The OSPs−CuBr catalyst has also shown easy availability, low cost, and high catalytic efficiency in a larger scale synthesis of 1,4-disubstituted 1,2,3-triazoles, which make it a valuable economical system as compared to the other catalysts reported earlier, and it shows great potential to being applied to the synthesis of them in industry. It can be recycled and reused at least eight times without a noticeable decrease in the product yield and its catalytic activity. As far as we know, it is the most efficient and cheapest approach for the synthesis of 1,2,3-triazoles. We hope this eco-efficient and green protocol may be of value for both synthetic as well as medicinal chemists for academic research and practical applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization of all the products by FTIR and ^1H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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