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Magnetic (Chitosan/Laponite)-Immobilized Copper (II) Ions: An Efficient Heterogeneous Catalyst for the Azide–alkyne Cycloaddition

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Abstract

The Cu^{2+} ions immobilized on a novel magnetic chitosan-based catalytic system by combination laponite RD was prepared. Cu^{II} -magnetic chitosan/laponite RD (Cu-mCSLap) nanocomposite was characterized by X-ray diffraction analysis, energy dispersive X-ray Analysis, scanning electron microscope and transmission electron microscope. Further, we tested the catalytic activity of this well-defined material in three-component CuAAC reactions to obtain 1,4-disubstituted-1,2,3-triazoles in good to excellent yields from an organic halide, sodium azide and alkyne under air in water as a green solvent.

Keywords: Chitosan; Laponite RD; Magnetic Catalysis; Copper (II); Azide–Alkyne Cycloaddition

1. Introduction

1,2,3-triazole derivatives have gained significant amount of attention due to their wide application in various fields, such as material science and biology, agricultural and pharmaceutical.¹⁻³ One of the most interesting synthetic tools for comfortable and trusty construction of 1,2,3-triazole derivatives is the 1,3-dipolar cycloaddition of organic azides and terminal alkynes in the presence of copper-containing catalysts.⁴ Although Cu(I)-

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catalyzed cycloaddition of azides and alkynes has been extensively reported, but in recent years, due to higher stability of Cu(II)-containing compounds and also their easy synthetic methods, they has characterized as a catalyst for the azide–alkyne cycloaddition.⁵⁻⁷

In order to prepare heterogeneous catalytic systems based on copper (II), an easy and efficient method is the immobilizing Cu²⁺ ion on solid supports ions on a solid support.⁸ In this regard, various solid supports including clays, polymers, magnetic nanoparticles, and alumina have been used for immobilizing Cu^{2+} ions.⁹⁻¹² From standpoints of non-toxicity. biodegradability, and natural origin, the polysaccharides such as chitosan and alginate with different functionalities are suitable candidates in designing Cu²⁺-loaded solid catalytic systems.^{13, 14} Chitosan is known as a basic polysaccharide carrying primary amine pendants. This biopolymer is derived from chitin (with a wide distribution in living organisms) by deacetylation method.¹⁵ The high affinity of amine groups to complex with Cu²⁺ ions makes the chitosan as a green candidate to fabricate solid catalytic systems.¹⁶ In spite of the high tendency of chitosan to bind with Cu²⁺ ions, the low mechanical and thermal properties restrict its applications in some catalytic systems.¹⁷ To overcome these disadvantages the nanoclays with high surface area can be used. The hydroxyl and amine functional groups on chitosan are interacted physically with hydroxyl groups of nanoclays such as montmorillonite.¹⁸ From a recovery and reusability standpoint, magnetic catalytic systems are recommended. Magnetic Fe₃O₄ nanoparticles are combined with the catalytic supports; therefore the magnetic materials can be easily separated from reaction media without needing filtration and centrifugation processes.¹⁰ The magnetic nanoparticles with homogeneous dispersing in catalytic systems without any aggregation are desirable. In this regard, magnetite nanoparticles can be immobilized on the laponite RD nanoclay with disc forming ability in water. Magnetic laponite RD discs are uniformly dispersed in the media due to the anionic centers on its structure.¹⁹

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The main objective of this work was to fabricate a novel magnetic chitosan-based catalytic system by combination laponite RD. The magnetic nanocomposite was prepared through in situ method. The Cu²⁺ ions were immobilized on the obtained nanocomposite. The 1,3-dipolar azide–alkyne cycloaddition reaction proceeds with Cu^{II}-magnetic chitosan/laponite RD nanocomposite with excellent yields.

2. Materials and Methods

2.1. Materials

Chitosan with ~85% of degree of deacetylation and molecular weight of 2500±30 kDa was obtained from Sigma-Aldrich and used without any purification. Laponite RD nanoclay was supplied from Southern Clay Products, USA (surface area: 370 m²/g, bulk density: 1000kg/m³, chemical composition: SiO₂ 59.5%, MgO 27.5%, Li₂O 0.8%, Na₂O 2.8%, loss on ignition: 8.2%).FeCl₃.6H₂O, FeCl₂.4H₂O, and CuSO₄.5H₂O chemicals were purchased from Merck (Germany) and used as received. Ammonia solution (NH₄OH, 25 %wt, Merck, Germnay) and sodium tripolyphosphate (TPP, Sigma-Aldrich, USA) were used as received.

2.2. In situ preparation of magnetic chitosan/laponite RD and its catalytic system

The aqueous dispersion of nanoclay with 1 %wt was prepared by adding 1 g of laponite RD in 100 mL distilled water, and then stirring the clay-dispersed solution for overnight with a magnetic stirrer (500 rpm). To ensure homogeneous dispersion of laponite RD, the solution was sonicated for 10 min (power: 70 W and frequency: 50 kHz; Bandelin, Sonoplus, HD 2200, Germany). Before adding the iron salts, the laponite solution was degassed by bubbling N₂ atmosphere for 30 min. Then, 2.22 g of ferric salt (FeCl₃) and 0.87 g of ferrous salt (FeCl₂) were dissolved in 20 mL distilled water and added immediately to the laponite solution. The solution was allowed to stir under N₂ gas for 10 min.

Chitosan solution was individually prepared by dissolving 1 g of its powder in 100 mL of 1 % wt of acetic acid solution. The obtained solution was added to the Fe^{2+}/Fe^{3+} -loaded laponite

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DOI: 10.1039/C6NJ03862J RD solution. The temperature of the mixture was adjusted at 60 °C under N₂ atmosphere condition and magnetic stirring at 500 rpm. The ammonia solution (NH₄OH, 3 M) was slowly added to the reaction mixture until the pH of the solution reached to 11. The produced dark magnetic nanocomposite was stirred at 60 °C for 1 h. In order to purify and neutralize the product, magnetic chitosan/laponite RD was thoroughly washed with excess distilled water. The purified magnetic nanocomposite was dispersed under ultrasound condition in water and the TPP (2 %wt, 5mL) was slowly added into magnetic solution in order to crosslink the magnetic chitosan/laponite RD (mCSLap) nanocomposite. The pH of resulting solution was reached to 5.5 by adding 0.1 M of HCl solution. The TPP-crosslinked nanocomposite was sonicated as above and the magnetic solution was divided into two parts. The first part was filtered and dried at room temperature and the dried product was kept in order to compare with the structure of catalyst. The second part was used for the preparation of the magnetic catalyst. The final volume of magnetic solution was 50 mL. For the preparation of catalyst, the 0.39 g of CuSO₄.5H₂O was dissolved in 50 mL distilled water and was added dropwise into magnetic chitosan/laponite RD solution at ambient temperature. The mixture was stirred on a shaker (120 rpm) for 5 h to reach equilibrium adsorption of Cu^{2+} ions on magnetic nanocomposite. Finally, the Cu-adsorbed nanocomposite was removed by a magnet and dried at room temperature. The supernatant was used for estimating the content of Cu²⁺ ions loaded in the magnetic sample. Therefore, 1 mL of supernatant was added to the 3 M of ammonia solution and the un-adsorbed concentration of Cu²⁺ ions was investigated at λ_{max} =600 nm by UV-visible spectrophotometer (UV-1800, Shimadzu, Japan). The amount of adsorbed copper (II) on magnetic nanocomposite was calculated from the difference between the initial concentration of the used copper (II) ions and the remained concentration of Cu²⁺ in the supernatant.

2.3. Characterization

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Fourier infrared (FTIR) spectra of dried samples were recorded by Bruker 113V FT-IR spectrometer (in KBr pellets). X-ray diffraction (XRD) patterns of dried and finely powdered samples were made on a Siemens D-500 X-ray diffractometer (Cu-K α , λ = 1.54 Ű, Voltage: 35 kV, current: 30 mA). After a thin layer coating of gold on dried samples, the surface morphology of magnetic nanocomposites was imaged on a scanning electron microscopy energy dispersive X-ray instrument (SEM/EDX, VEGAII, XMU, Czech Republic). The wet nanocomposites were dispersed in ethanol and transmission electron microscopy (TEM) images were studied on a Philips CM10 operating at 60 kV tension. The magnetic properties of the magnetic samples were recorded on a vibrating sample magnetometer (VSM) (model 7400, Lakeshare Company, USA).

Results and Discussion Synthesis and characterization

Fig. 1 shows the preparation of magnetic catalyst by combination of chitosan and laponite RD. A solution of Fe^{2+}/Fe^{3+} ions was added to the dispersed laponite RD solution and was allowed to interact the iron ions electrostatically with laponite RD discs. The exchange between the interlayer Na⁺ ions of laponite RD and the iron ions can be occurred easily.²⁰The chitosan solution was poured to the iron-loaded clay solution and subsequently, by adjusting the pH of mixture at 11 by the ammonia solution the magnetic nanocomposite was obtained. The TPP, a common crosslinker in the preparation of chitosan-based materials, was used to obtain the crosslinked magnetic nanocomposite.²¹Because of the high tendency of chitosan and laponite RD to complex with Cu²⁺ ion, copper (II) solution was added to the magnetic nanocomposite.^{22, 23} A greenish Cu²⁺-loaded magnetic chitosan/laponite RD catalyst was gained. The adsorption capacity of magnetic nanocomposite for Cu²⁺ ions was calculated and found to be 365 mgg⁻¹. The resulting catalyst was loaded with the high contents of Cu²⁺ ions

and was comparable with the other supports used for the preparation of Cu^{2+} -loaded catalysts.^{10, 11}



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Fig. 1 A simple scheme showing the steps used for the preparation of Cu²⁺-chitosan/laponite RD (Cu-mCSLap) catalytic system.

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TEM micrographs of the mCSLap and Cu-mCSLap were used to investigate the formation of nanoparticles in nanocomposites. Disc-like nanoplates can be formed by dispersing and swelling the laponite RD in water (thickness: 1 nm and diameter: 25-40 nm).²⁴ The main advantage of the synthesis of magnetic nanoparticles in the presence of laponite RD disc is the formation of magnetite embedded within the laponite discs. This phenomenon prevents the aggregation and clustering of magnetic nanoparticles.¹⁹ As shown in Fig.2a, in the absence of Cu²⁺, the magnetic laponite RD showed disk-like nanoplates in shape with an average size of 29 ± 4 nm. A similar observation has been reported in the preparation of clay-based hydrogels using laponite disk-like nanoplates.²⁵ Additionally, the nanoparticles with the size of less than 20 nm are visible in the polymer matrix that can be assigned to the formed magnetic Fe₃O₄ nanoparticles freely. The Cu-mCSLap indicated no deformation or aggregation in the magnetic nanoparticles and the morphology was obtained similar to the mCSLap nanocomposite (Fig. 2b).



Fig. 2 TEM images of (a) Cu^{2+} -unloaded (mCSLap) and (b) Cu^{2+} -loaded (Cu-CSLap) nanocomposites.

The surface morphology of mCSLap and Cu-mCSLap catalyst was studied by SEM technique. The results revealed a coarse and undulant structure for mCSLap and no spherical discs or nanoparticles due to the magnetic laponite RD was observed; indicating uniform dispersion of magnetic clay in nanocomposite matrix (Fig. 3a). By loading the Cu²⁺ ions, the surface structure of nanocomposite was changed slightly, and a nodule-like surface was

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obtained (Fig. 3b). Compared to the mCSLap nanocomposite, the variation in surface of catalyst can be attributed to the crosslinking of the chitosan backbones through adsorption of Cu^{2+} ions. The energy dispersive X-ray spectroscopy (EDX) analysis of mCSLap indicated Fe and Si confirming the magnetic laponite RD (Fig. 3a). In the EDX spectrum of magnetic catalyst the Cu characteristic peak was appeared and confirmed the presence of copper ions in the catalyst (Fig. 3b).



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Fig. 3 SEM/EDX of (a)mCSLap and (b) Cu-CSLap nanocomposites.

The d_{001} peak in XRD diffractograms is indicative the interaction/exfoliation structure of nanoclays in polymer matrix. From the XRD pattern, a distinctive diffraction peak for native laponite RD with d-spacing of 12.77Å (20=6.4°) was clearly observed (Fig. 4a). The XRD

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pattern of neat chitosan showed a characteristic peak at $2\theta=20^{\circ}$ that is attributed to the partial crystalline structure of chitosan. Moreover, chitosan showed a broad peak at $2\theta=10.5^{\circ}$, originating from the hydrated crystals of α -chitin chains remaining in raw chitosan. The XRD diffractograms of nanocomposites mCSLap and Cu-mCSLap were studied and shown in Fig.4a. Both of them indicated similar patterns. By synthesizing magnetite in the presence of laponite RD and chitosan, the intensive peak of clay at $2\theta=6.4^{\circ}$ was disappeared, showing exfoliation of clay nanoparticles as confirmed in TEM micrographs. Also, the characteristic peak of chitosan at $2\theta=20^{\circ}$ was vanished, showing the amorphous structure of chitosan in nanocomposite matrix. The existence of the magnetite in the nanocomposites was evidenced by the distinctive peaks at about $2\theta=30.4^{\circ}$, 35.6° , 43.5° , 53.2° , 57.4 and 63.3° .²⁶The X-ray diffractions of mCSLap and Cu-mCSLap revealed that the produced magnetite nanoparticles have high crystalline and spinel structures. After loading the Cu²⁺ ions, the intensity of distinctive peaks of Cu-mCSLap was slightly reduced in compared to the mCSLap, in which can be attributed to the non-magnetic behavior of copper (II) ions.

The magnetic behavior of magnetic mCSLap and Cu-mCSLap nanocomposites were investigated with a VSM technique at 298 K and in a range of applied field of ±8 kOe (Fig.4b). The hysteresis loops of mCSLap and Cu-mCSLap nanocomposites showed superparamagnetic behavior that is obvious from zero value for the coercivity and remanence on the magnetization curves. The saturation magnetization was reduced from 3.8 emu/g for mCSLap to 2.7 emu/g for Cu-mCSLap. The corresponding reduction in the magnetization of catalyst in compared to the neat nanocomposite can be assigned to the antimagnetic behavior of loaded copper (II). As illustrated in insert of Fig. 4b, the magnetization of catalyst was sufficient to remove it from aqueous solution by a permanent magnet.

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Figure 4 (a) XRD patterns of chitosan, neat laponite RD, mCSLap, and Cu-mCSLap nanocomposites; (b) room-temperature magnetization curves of mCSLap and Cu-CSLap nanocomposites; (c) FTIR spectra of initial materials, mCSLap, and Cu-CSLap.

The FTIR spectra of chitosan, pristine laponite RD, magnetic laponite RD, mCSLap, and CumCSLap were investigated and shown in Fig.4c. In chitosan spectrum, the absorption bands at 1658, 1560, and 1084 cm⁻¹ correspond to the amide I, amide II, and glycosidic bonds, respectively. The characteristic peaks of pristine clay are as follow: the hydroxyl groups and the adsorbed H₂O on the laponite RD displayed a broadband, visible in the range of 3000-3700 cm⁻¹;3643cm⁻¹(stretching vibration of Si-OH), 3687 cm⁻¹ (stretching vibration of Mg-OH bonds), 998 cm⁻¹ due to the stretching vibration of Si-O and Si-O-Si bonds, and 464 cm⁻¹ owing to the vibration stretching of Mg-O. For a detailed comparison, the FTIR spectrum of magnetic laponite RD was shown in figure. The magnetic laponite RD showed almost all characteristic bands of the pristine laponite RD, with slight peak shifts to the lower

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frequencies. The distinctive peaks of Fe-O in Fe₃O₄/laponite RD (450 and 470 cm⁻¹) were not distinguishable due to the overlap with characteristic peak of laponite RD at around 466 cm⁻¹. In the mCSLap nanocomposite, the absorption bands of the amide I, amide II, and glycosidic bonds related to the chitosan were appeared at 1625, 1535, and 1065 cm⁻¹, respectively. In comparison to the neat chitosan, the peaks showed a shifting to the lower frequencies, confirming the interaction between chitosan and magnetic laponite RD. The presence of magnetic clay in mCSLap is evident by the bands at 1006 cm⁻¹ (stretching vibration of Si-O and Si-O-Si bonds) and 444 cm⁻¹ (Fe-O in Fe₃O₄/laponite RD). The Cu-loaded catalyst, Cu-CSLap, showed almost the characteristic peaks of mCSLap nanocomposite with a slightly shifting to the higher frequencies.

3.2.Catalytic effects

The Cu^{II}-magnetic chitosan/laponite RD nanocomposite demonstrated to be very efficient in the multicomponent 1,3-dipolar cycloaddition of terminal alkynes and organic azides yielded in situ from different organic halides and sodium azide. Phenylactelylene and benzyl chloride were chosen as model starting compounds for the optimization of the reaction conditions (Table 1). Initially optimization of the cycloaddition reaction was performed by varying the catalyst amount. As shown in Table 1, after 12 h no product was obtained in the absence of a catalyst (entry 1). The best result was achieved with0.004 g of the catalyst (entry 4). With a further increase of the catalyst amount to 0.005 g showed adverse effect on the product yield (entry 5). The yield of cycloaddition product 1- benzyl-4-phenyl-1H-1,2,3-triazole, monotonously increased with increasing reaction temperature to 70 °C (entries 6-8).Interestingly, from the different solvents checked, H₂O as was found to be more effective for this reaction than CH₃OH, CH₃Cl, ethyl acetate, CH₃CN and acetone (entries 4 and 9-13). The cycloaddition reaction of phenyl acetylene with benzyl chloride and sodium azide gave product almost quantitatively in 4 hour of reaction time (entry 15).

Entry	Amount of	Solvent	Temperature	Time	Yield
-	catalyst		(°C)	(h)	(%) ^a
	(g)				
1	-	H ₂ O	70	12	0
2	0.002	H_2O	70	12	70
3	0.003	H_2O	70	12	80
4	0.004	H_2O	70	12	97
5	0.005	H2O	70	12	76
6	0.004	H_2O	rt	12	15
7	0.004	H_2O	50	12	69
8	0.004	H_2O	60	12	94
9	0.004	CH ₃ OH	70	12	81
10	0.004	CH ₃ CN	70	12	trace
11	0.004	EtOAc	70	12	trace
12	0.004	CHCl ₃	70	12	trace
13	0.004	acetone	70	12	58
14	0.004	H_2O	70	2	94
15	0.004	H_2O	70	4	97

Table 1.	The Ef	ffect of v	various	conditions	on the	azide-	-alkyne	cyclo	oadditi	on
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^aIsolated yield

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In order to produce the 1,4-disubstituted-1,2,3-triazoles, the same process was successfully applied to a wide range of diversely substituted phenyl acetylenes and a mixture of benzyl bromides/chlorides with sodium azide. The results of cycloaddition reaction are summarized in Table 2. With substitution of electron withdrawing or electron donating groups on the phenyl ring of the phenyl acetylenes and benzyl halides, no significant influence on the yield of the reaction was observed. But ortho substituents on the benzyl chloride in compared to the para derivative showed minor steric hindrance (entries 2 and 3). Aliphatic alkynes required longer reaction times than aromatic alkynes to give high yields of the corresponding cycloaddition reactions (entries 7 and 8). Replacement of benzyl bromide with benzyl chloride showed a conclusive effect on the catalytic activity, as benzyl bromide reacted to give the corresponding 1,2,3-triazole products in essentially quantitative yields (entries 9-11), except for aliphatic alkynes containing -OH group (entries 12 and 13).

Table 2 Cycloaddition of alkyl halides with terminal alkynes in the presence of Cu^{II} -magnetic chitosan/laponite RD nanocomposite

R ₁ —	X + NaN ₃ + R ₂	H ₂ O, 70 °C	N N
			R ₂
Entry	Aliphatic halide	Alkyne	Yield $(\%)^a$
1	CI		97
2	CI		90
3	H ₃ C Cl CH ₃		76
4	CI	————————————————————————————————————	93
5	CI	MeO-	91
6	CI	H ₃ C-	93
7	CI	HO HO	54
8	CI	но	60
9	CI		97
10	Br		97
11	Br	MeO-	95
12	Br	H ₃ C-	92



^aIsolated yield

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The worthiness and efficiency of the present Cu-CSLap nanocomposites are shown by the comparison of the catalytic behavior of Cu-CSLap nanocomposites with previously reported copper catalysts (Table 3). The catalytic reactivity of Cu-CSLap nanocomposites is superior to the reaction conditions, such as much amount of catalyst (entries 2 and 4), using of hazardous solvents (entry 3) and addition of an additive agent (entries 3 and 5). Also, easy separation and recoverability of catalyst and in situ generation of organic azides are other advantages of our catalytic system.

Table 3. Comparison of the catalytic reactivity of Cu-CSLap nanocomposites with other reported catalysts

Entry	Catalyst	Conditions	Yield	Ref.
	-		(%)	
1	Cu-CSLap nanocomposites	0.004 g catalyst/ H ₂ O/12 h/70 °C	97	Present work
2	POSS–SAL–Cu	0.01 g catalyst/ H ₂ O/12 h/70 °C	95	27
3	Cu NPs/aminopropyl-silica	0.004 g catalyst/PhNHNH ₂ /THF/2h/	38	28
		25 °C		
4	Cu/CeO ₂	0.006 g catalyst/H ₂ O/4 h/70 °C	96	29
5	Kenaf cellulose supported	0.001 g catalyst/H ₂ O/sodium	94	30
	poly(hydroxamic acid) Cu ^{II} -	ascorbate (5 mol%)/ 4 h/70 °C		
	complex			

4. Conclusion

In summary, the present study illustrates the feasibility and applicability of utilizing the Cu^{II}magnetic chitosan/laponite RD nanocomposite to catalyze the 1,3-dipolar cycloaddition of terminal alkynes with organic azides generated in situ from sodium azide and different organic halides for the synthesis of the corresponding 1,2,3-triazoles. The process is environmentally friendly and uses an easily available solvent to produce excellent yields.

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The present work reports the synthesis and characterization of Cu^{2+} -loaded magnetic chitosan/laponite catalytic system. Under green protocol and using water as a solvent, CuAAC reactions were successfully performed to obtain 1,4-disubstituted-1,2,3-triazoles in good to excellent yields.