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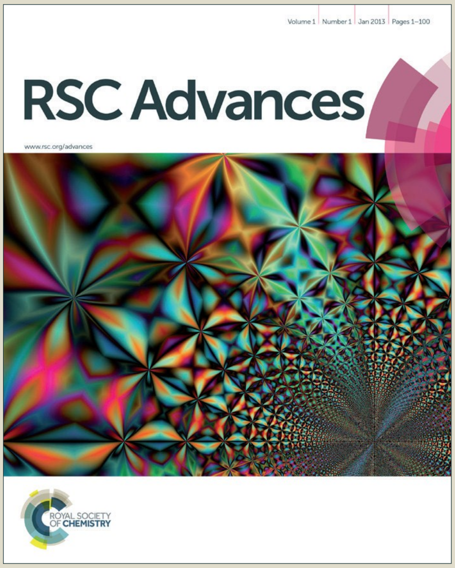

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Ecofriendly synthesis of heterogeneous polyvinyl alcohol immobilized copper (II) Schiff base complex as an efficient, reusable catalyst for one-pot three component green preparation of 5-substituted 1*H*-tetrazoles under mild conditions

Milad Kazemnejadi[a] and Ali Reza Sardarian[*b]

A new heterogeneous and reusable polyvinyl alcohol immobilized copper (II) Schiff base complex (PVA@Cu(II) Schiff base complex) was synthesized in water, characterized and used for highly efficient environmentally benign one-pot three component preparation of 5-substituted 1*H*-tetrazole derivatives through the click reaction of aliphatic and aromatic aldehydes with hydroxylamine hydrochloride and azide salt as inexpensive and commercially available substrates in water and very short reaction times at room temperature.

Introduction

Tetrazoles are an important class of heterocyclic nitrogen-rich compounds, due to their wide range of applications in agriculture, pharmacy, medicine, chemistry and material sciences. So the preparation of various tetrazole derivatives over the past few years has been growth rapidly.[1] In pharmacy, they are employed as antidiabetics,[2] antibiotics[3] and HIV-inhibitor.[4] Owing to lower toxicity and higher lipophilicity of tetrazoles, they can be used as isosteric replacements in drugs.[5] Furthermore, in coordination chemistry they have noteworthy task as a ligand. [6]

There are several strategies for preparation of 5-substituted 1*H*-tetrazoles, in which the [3+2] cycloaddition reaction between nitriles and azide salts has been as a popular method.[7]

Several procedures of this strategy, which have been recently reported in the literature, are: a) R-CN, NaN_3, DMF, I_2, 120 °C,[8] b) R-CN, NaN_3, $Et_3N.HCl$, $PhNO_2$, MW, 100 °C,[9] c) R-CN, NaN_3, $Et_3N.HCl$, DMF, 130 °C, MW,[10] d) R-CN, NaN_3, $AlCl_3$, NMP, MW, 200 °C,[11] e) R-CN, NaN_3, TMSCl, NMP, MW, 220 °C,[12] f) R-CN, NaN_3, water, $ZnBr_2$ or AcOH,[13] g) R-CN, NaN_3 tetrabutylammonium hydrogen sulfate in water,[14] h) R-CN, NaN_3, NMP, water,[15] i) R-CN, NaN_3, isopropanol, water, $Sc(OTf)_3$,[16] j) R-CN, NaN_3, immobilized $AlCl_3$ on Al_2O_3, DMF,[17] k) R-CN, NaN_3, immobilized copper(II) complex of 4-phenyl-2,2':6',2"-terpyridine on activated multi-walled carbon nanotubes, DMF,[18] and l) ArCN, NaN_3, DMF, $Fe_3O_4@SiO_2$/ salen complex of Cu(II), 120 °C.[19a]

Due to more availability and less toxicity of aldehydes in compare to nitriles and high efficiency of copper catalysts in [3+2]-cycloaddition reactions,[19] using copper catalysts for preparation of 5-substituted 1*H*-tetrazoles through the reaction of a mixture of aldehydes and hydroxylamine hydrochloride or oximes with NaN_3 have been drawn attention of organic chemists in last few years. Patil and his co-workers employed $Cu(OAc)_2$ as a catalyst for preparation of 5-substituted 1*H*-tetrazoles from oximes and NaN_3 in DMF at 120 °C.[20] Heravi and his co-workers applied also $Cu(OAc)_2$ to synthesize of 5-substituted 1*H*-tetrazoles *via* the reaction of aldehydes, hydroxylamine and $[bmim]N_3$ (bmim = 1-butyl-3-methylimidazolium azide), in DMF at 120 °C.[21]

Recently, Abdollahi-Alibeik and his co-worker have reported a new catalyst, Cu-MCM -41 (MCM = Mobile Composition of Matter) nanoparticles for preparation of this type of tetrazoles from the reaction of aldehydes, hydroxylamine and NaN_3 in DMF at 140 °C.[22]

Majority of methods, which have been above-mentioned, suffer some drawbacks such as need to use high temperature and toxic and expensive solvents.

For sake of notable property of tetrazoles and catalytic activity of copper for the formation of N-containing heterocyclic compounds[23], herein, we wish to introduce, a novel, recoverable and reusable heterogeneous catalyst to overcome some of the above-mentioned impediments by working under mild and green conditions to perform efficiently preparation of 5-substituted 1*H*-tetrazoles derivatives (Scheme 1).

Experimental

Synthesis of PVA@Cu(II) Schiff base complex (5)

Initially, for preparation of Schiff base ligand **4** (Scheme 2), polyvinyl alcohol (PVA, purchased from ACROS Organics., degree of polymerization = 500, Mw~22000) (0.2 g) was added to 20 mL water as a green solvent in a 50 mL round bottom flask at 70 °C and stirred for 20 min to dissolve PVA completely . Then 0.5 mL (5 mmol) epychlorohydrin (ECH) was added to the reaction mixture (a biphasic solution mixture was formed at beginning) and refluxed in 80 °C for 12 h along with stirring. The precipitated product **2** (Scheme 2) was simply filtered, washed with cold acetone (2 × 10 mL) and dried to give the pure product **2**. Then the product **2** and ammonium chloride salt (0.30 g, 5.60 mmol) were dissolved in 20

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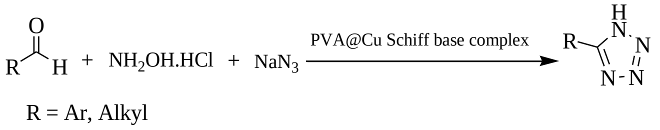
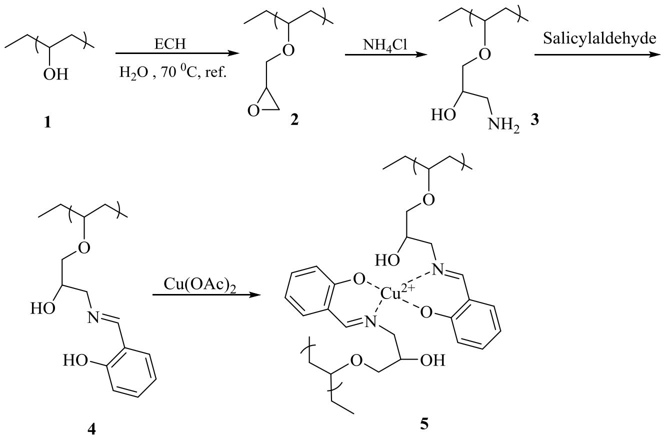
mL of water at 70 °C and then the resultant reaction mixture was refluxed in 80 °C for 12 h to obtain the product **3** (Scheme 2).



Scheme 1 Preparation of 5-substituted 1*H*-tetrazole by using of PVA@Cu(II) Schiff base complex (catalyst)



Scheme 2 Preparation of PVA@Cu(II) Schiff base complex

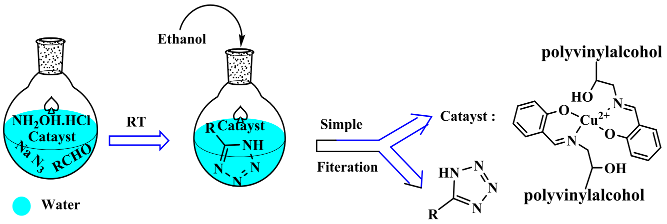
The precipitated product **3** by addition of acetone (10 mL) was filtered, washed with cold acetone (2 × 10 mL) and dried to provide the pure product (as a white powder). The product **3** was transferred to a 50 mL round bottom flask along with addition of 20 mL of water: ethanol (1:1) and then salicylaldehyde (1.2 mL, 11.3 mmol) was added to the reaction mixture and stirred for 2 h. To the yellow viscose mixture formed, because of formation the corresponding Schiff base **4**, $Cu(OAc)_2$ (0.9 g, 4.9 mmol) was added gradually in 5 min to the reaction mixture to obtain PVA@Cu(II) Schiff base complex **5** (Scheme 2) as a bright green solid. The polymeric copper complex was purified by simple filtration and washing with cold acetone (2 × 10 mL) to provide the pure complex (0.93 g).

It was also possible to prepare PVA@Cu(II) Schiff base complex in DMSO as same procedure as described above.

Formation of the complex **5** was monitoring with UV-Vis instrument at different period of times.

General procedure for preparation of 5-substituted 1*H*-tetrazoles

A mixture of aldehyde (1 mmol), sodium azide (0.10 g, 1.50 mmol), hydroxylamine hydrochloride (0.10 mg, 1.5 mmol) in water (5 mL) was stirred in the presence of PVA@Cu(II) Schiff base complex as a catalyst (10 mg, 0.43 mol%) for sufficient time (Generally less than 15 min), which was required for completion of the reaction. After completion of the reaction, filtration of the reaction mixture left a solid on the filter. For removal of soluble impurities entrapped in the solid, it was washing with water (5 mL). Then the solid was extracted with 10 mL (2 x 5 mL) of hot ethanol (50 °C) to separate the tetrazole product and leave the catalyst **5** as bright green solid, which could be reused without any purification for the next reaction (Scheme 3). Evaporation of filtrate provided the pure product.



Scheme 3 A Schematic processes for preparation of 5-substituted 1*H*-tetrazoles

Characterization instruments

FT-IR spectra of the tetrazole products, in form of KBr pellets, provided on Shimadzu FT-IR 8300 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Bruker avance DPX 250 MHz spectrometer using $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal reference. UV-Vis analyses performed on UV Spectrolab BEL photonics in dimethyl sulfoxide (DMSO) as solvent. Thermal studies (TGA-DTG) have been performed on a NETZSCH STA 409 PC/PG in nitrogen atmosphere with a heating rate of 20 °C/min in the temperature range of 25-600 °C. ICP analysis was performed by VARIAN VISTA-PRO CCD simultaneous ICP OES instrument.

Analytical data for 5-[4-(N, N-dimethylphenyl)]-1*H*-tetrazole (4b)

White solid, M.P. 132-134 °C. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 2.91 (s, 6H), 6.60 (d, 2H, *J* = 8.75), 7.37 (d, 2H, *J* = 8.75). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) = 40.2, 11.9, 119.6, 128.3, 150.3, 151.5. IR (KBr): $\upsilon(cm^{-1})$ = 570, 739, 1064, 1188, 1527, 1612, 2808, 3263. CHN: Found %: C 56.80; H 5.33; N 37.01. $C_9H_{11}N_5$. Calculated, %: C 57.13; H 5.86; N 37.01.

Results and discussion

Catalyst characterization

Preparation of PVA@Cu(II) Schiff base complex was monitoring with FT-IR instrument in each stage.

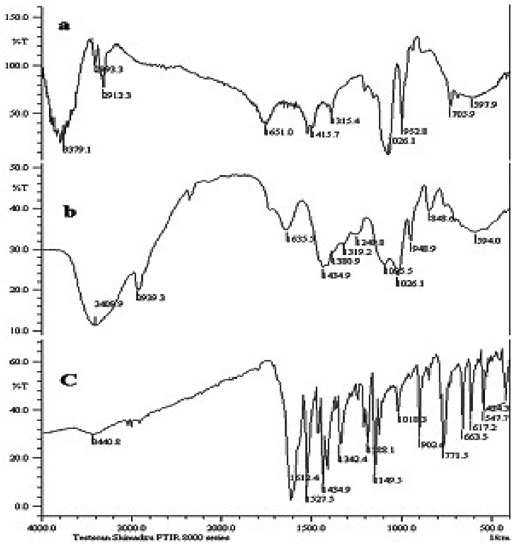


Fig 1 FT-IR spectrum of PVA epoxidized (a), polymeric Schiff base ligand **4** (b) and its complex **5** (c)

In FT-IR spectrum of the epoxide product of PVA with ECH, the presence of peaks at 848, 948 and 1026 cm^{-1} was belonged to the epoxy group. The red shift of the peak at 1635 cm^{-1} to 1612 cm^{-1} was due to the chelating of copper in polymeric Schiff base ligand **4** that was shown in Fig. 1.

^1H NMR spectrum of the PVA ligand was recorded in DMSO-d_6 as solvent and TMS as internal reference. Advent of peak at 9.430 pp m in ^1H-NMR demonstrated the preparation of iminium bond in the polymeric Schiff base ligand **4**. The chemical shift related to aromatic bonds is setting in 5.6-7.5 ppm (Fig. 2).

Regarding to Zabierowski and co-workers report[24] about determination of the structure of salicylidene-2-ethanolamine Schiff bases of copper(II) complex by X-ray, Fig. 3, in which copper(II) atoms are in N_2O_2 coordination environment of two chelating ligands, the structure of PVA@Cu(II) Schiff base complex **5** might be most likely as it is as shown in scheme 2.

Formation of the complex was also investigated with UV-Vis technique in 5 and 45 min after addition of $Cu(OAc)_2$ into solution of polymeric ligand **4** in DMSO (Fig. 4). Appearance of a peak near to 400 nm that was related to electron transfer of Cu (d-d; metal to ligand charge transfer (MLCT)) and also elimination of the absorption at 310-350 nm, which is due to $\pi \rightarrow \pi^*$ of nitrogen atom in C=N bond in **4,** demonstrated the chelation formation of $Cu(OAc)_2$. Also a broad adsorption for polymeric Schiff base ligand **4** at ~ 300-350 that assigned to $n \rightarrow \pi^*$ of imine (C=N) have been eliminated due to chelation to Cu(II).

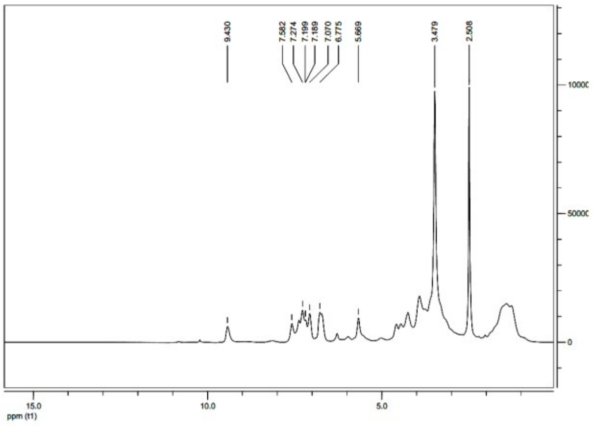


Fig 2 ^1H NMR spectrum of iminium polymeric ligand based on PVA

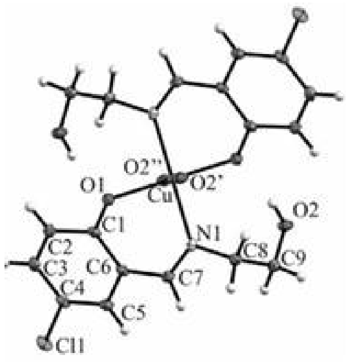


Fig 3 Molecular structure of bis{4-chloro-2-[(2-hydroxyethyl) iminomethyl]-phenolato}-copper(II) $[Cu(cheimp)_2]$ [24]

Thermal stability of PVA@Cu(II) Schiff base complex **5** was shown in Fig.5. TGA-DTG spectrum represented three main weight loss stages: first at 110-220 °C corresponds to -9.12 % weight loss, which was belong to decomposition of ligand from PVA, second at 238-322 °C that showed decomposition of PVA. Third and final stage, which lasting to 600 °C, could be due to oxidation of copper and formation of CuO and carbonization of polyvinyl alcohol. Furthermore, a low weight loss in the beginning of the spectrum (Fig. 5, -2.27 %) showed escaping of humidity and solvent[25] trapped in polymeric complex.

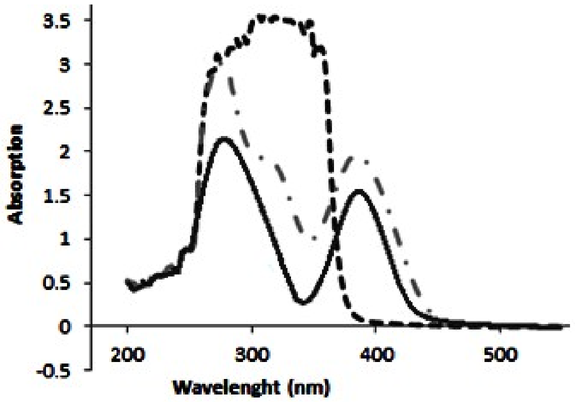


Fig 4 UV-Vis absorption of **4** (dash line) and the reaction mixture in 5 minutes (dash-dotted line) and 45 minutes (solid line) after addition of $Cu(OAc)_2$

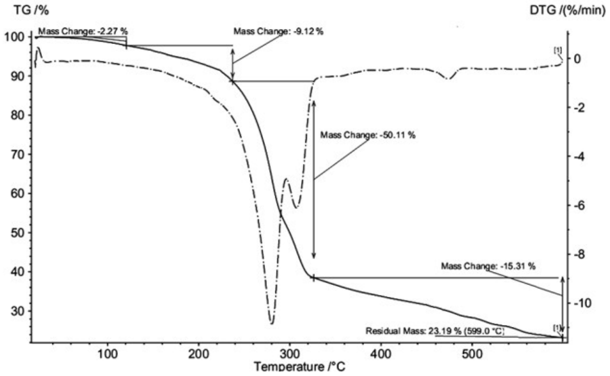


Fig 5 TG-DTG spectrum of **5** in nitrogen atmosphere by rate heating of 20°C/min

Table 1 Results from ICP analysis[a]

Sample	Conc. (mg/L)	Int. (C/S)
water	0.00	8.93
Cu-2.5	2.50	1672.38
Cu-5	5.00	3916.16
Cu-10	10.00	9191.00
Cu-20	20.00	18757.60
Cu-sample	27.30	51941.60
Cu-sample-5th run[b]	0.50	634.40

[a] The analyses were taken at 324.754 nm. [b] Analysis of residual reaction mixture after 5th run to elucidation of leaching amount of copper from catalyst **5**.

Loading amount of copper in catalyst **5** was determined by Inductive coupled plasma (ICP) experiment. Catalyst **5** (100 mg) was digested in H_2SO_4:HNO_3 (8:2, 10 mL) mixture (room temperature, 2 h) then diluted as 1:50 with distilled water and along with a blank (water) and four standards ($[Cu(OAc)_2]$; 2.5, 5, 10, 20 mg/L) were used for measuring of copper content in **5**. Experiments showed that 27.30 mg (27.3 wt%) copper was loaded on PVA ligand **4**, that was 4.3 mmol. g^{-1} (For 100 mg of **5**) (Table 1).

Optimization steps

For optimization of the reaction parameters, the reaction of benzaldehyde, hydroxylamine hydrochloride and sodium azide was chosen as a model reaction in the presence of PVA@Cu(II) Schiff base complex **5** as a catalyst. Then, the effect of solvent, temperature and amount of the catalyst was determined (Table 2), which the model reaction gave the best result when it was performed in water and at room temperature in the presence of 10 mg (0.43 mol %) of catalyst (Table 2, entry 1).

To elucidation of catalytic activity of PVA@Cu(II) Schiff base complex, the model reaction was carried out in presence of polyvinyl alcohol alone under the optimized conditions that were achieved before. Clearly, the reaction did not show any notable progress for PVA (Entry 9). Also the reaction did not proceed at all under the optimized conditions (Water medium and room temperature) in the presence of Cu(OAc)$_2$ as a catalyst (Table 2, entry 10).

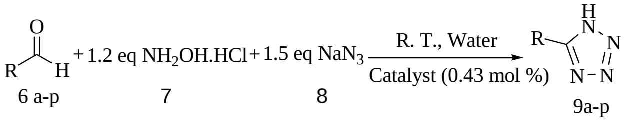
After implement of optimization steps, the catalyst was employing for determination of scope and versatility of the preparation of 5-substituted 1*H*-tetrazole derivatives under the optimized conditions. Various aromatic and aliphatic aldehydes served as substrate and the related results showed in table 3. Aromatic aldehydes bearing whether electron donating or electron withdrawing groups showed excellent results except in the case of 3,4-dihydroxy benzaldehyde and salicylaldehyde that afforded 70 % and 80 % yields respectively (Entries j and h). Aliphatic aldehydes, such as 3-phenyl propionaldehyde and lauraldehyde were also carried out the reaction and provided the desired products in high yields (Table 1, entries n and p) respectively.

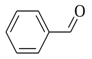
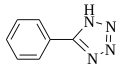
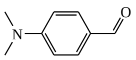
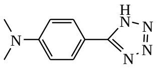
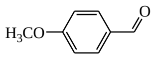
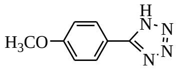
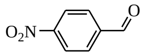
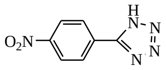
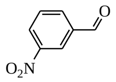
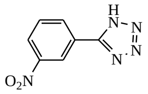
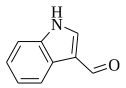
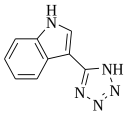
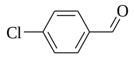
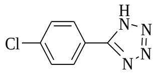
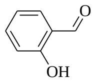
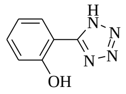
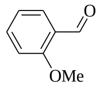
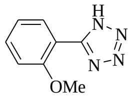
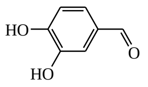
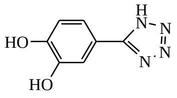
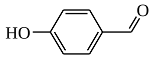
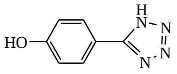
Table 2 Investigation of the reaction parameters for preparation of 5-phenyl-1*H*-tetrazole[a]

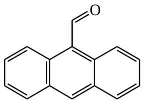
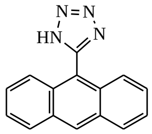
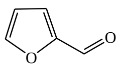
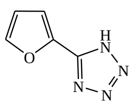
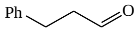
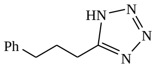
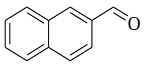
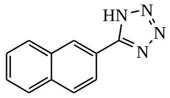
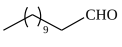
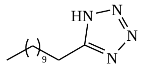
Entry	Solvent	Temperature (°C)[b]	Catalyst (mol %)	Time[c] (min.)	Yield (%)
1	H_2O	R. T.	0.43	7	98
2	H_2O	R. T.	0.8	7	98
3	EtOH	R. T.	0.8	60	25
4	EtOH	80	0.8	60	35
5	MeOH	R. T.	0.8	60	30
6	DMF	80	0.8	30	50
7	CH_3CN	80	0.8	30	45
8	Et_2O	R. T.	0.8	60	20
9	H_2O	R. T.	_[d]	60	Trace
10	H_2O	R. T.	25[e]	240	0

[a] Reaction condition: Aldehyde (1 mmol), hydroxylamine hydrochloride (1.5 mmol), sodium azide (1.5 mmol), solvent, temperature. [b] For optimization various temperatures were used for each solvent and just some cases were shown. [c] Completion of the reactions were monitored by TLC. [d] The reaction was done in the absence of **5** and in the presence of PVA alone. [e] The reaction was carried out in the presence of Cu(OAc)$_2$ (25 mol%) according to Patil and his co-workers report.[26]

Table 3 Synthesis of 5-substituted 1*H*-tetrazoles catalysed by PVA@Cu(II) Schiff base complex **5**[a]



Entry	Aldehyde	Product	Time (min)	Yield (%)[b]	M. P. (°C)[Lit.]
a			7	98	217-219[25]
b			5	98	132-134
c			7	98	233-234[27]
d			15	98	220-222[28]
e			15	97	155-157[29]
f			12	98	161-163
g			7	98	257-259[30]
h			15	80	219-221[31]
i			5	98	154-156
j			5	70	213-215
k			7	88	232-235[32]

l			8	95	148-150
m			8	98	220-222[33]
n			12	80	98-100[34]
o			5	95	205-207[8]
p			3	80	215-217

[a] Reaction condition: Aldehyde (1 mmol), hydroxylamine hydrochloride (1.5 mmol), sodium azide (1.5 mmol), water, room temperature, catalyst **5** (10 mg, 0.43 mol%). [b] Isolated yields

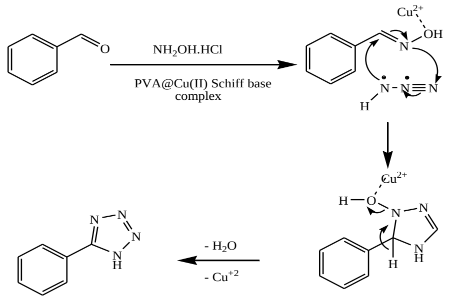
Mechanism studies

The literature review showed there are two general ways for preparation of 5-substituted-1*H*-tetrazoles from aldoximes in the presence of Cu(II) catalysts. In the first method, aldoxime is converted to the corresponding nitrile[20] and then to tetrazole *via* reaction with sodium azide[26] and in the other route, aldoxime or a mixture of aldehyde and hydroxylamine hydrochloride is transformed to the desired tetrazole by reaction with sodium azide.[20]

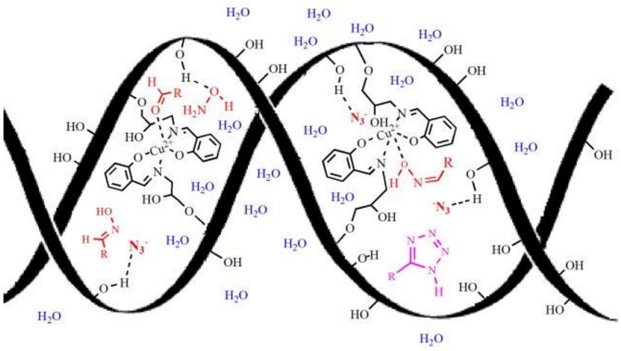
Therefore, for understanding the mechanism of performance of catalyst **5**, three reactions were designed to be studied: a) in the first reaction, salicylaldehyde reacted with hydroxylamine hydrochloride in the presence of catalyst **5** in water, which immediately provided salicylaldoxime in quantitative yield. In second experiment, conversion of salicylaldoxime to 2-hydroxybenzonitrile was checked in the presence of the Cu(II) catalyst **5**, which did not take place at room temperature and even higher temperatures in water. Finally, reaction of salicylaldoxime with sodium azide, which was proceeded rapidly in 11 min towards 5-(2-hydroxyphenyl) 1*H*-tetrazole in the presence of the catalyst **5** at room temperature in water.

The results of these studies demonstrated that in the present protocol, probably, oxime formation is followed by a [3+2] cycloaddition reaction between oxime and hydrazoic acid and then water elimination, on the base of Patil's report,[25] to be led to the title tetrazoles (Scheme 4).

On the other hand, due to the presence of both lipophilic (including C-C and C-H bonds) and hydrophilic parts (including polar groups and copper complex) in the structure of catalyst, it may act as a media that is able to dissolve all of the starting materials and keep them close together by hydrogen bonding and coordination with copper (II). Therefore, it provides effective concentrations of the starting materials as higher as possible to help the reaction proceeds without need to large amount of energy and take places at room temperature (Scheme 5)



Scheme 4 Contingent mechanism for tetrazole synthesis PVA@Cu(II) Schiff base complex **5** as a catalyst



Scheme 5 A simple and brief schematic of probable performance of the catalyst **5**.

Retrieval and reusability of the catalyst

One of the most significant features of a catalyst is its ability for resumption and thermal stability. Thus, we checked the reusability and recoverability of the catalyst **5** in the model reaction under the optimized reaction conditions after separation of the catalyst from the reaction mixture by convenient filtration. According to the data presented in table 4, the catalyst was reusable for four consecutive runs without any considerable weight and reactivity loss. A pronounce loss of activity was observed in 5th run and analysis of the filtrate after 5th with ICP showed the presence of 0.50 mg (18.31 %) copper in residual solution because of leaching phenomenon.

For comparison among of efficiency of PVA@Cu(II) Schiff base complex with the reported catalysts in the literature for preparation of 5-substituted-1*H*-tetrazole, the reaction of benzaldehyde with hydroxylamine hydrochloride and azide salt was selected as the model reaction. The results exhibited in table 5 appeared superiority of PVA@Cu(II) Schiff base complex over the other systems in point of view of environmental and economical aspects.

Table 4 Retrieval and recoverability of PVA@Cu(II) complex

Run	Catalyst Yield (%)	Product Yield (%)
1	98	98
2	98	98
3	97	95
4	95	95
5	82	90

Table 5 Comparison among efficiency of PVA@Cu(II) Schiff base complex with the reported catalysts in the literature for preparation of 5-phenyl 1*H*-tetrazole

Catalyst	Solvent/ T (°C)	Time (h)	Yield (%)	Ref.
$Cu(OAC)_2$ (15.0 mol%)	DMF/ 120	12	96	21
Cu-MCM-41 (0.05 mol%)	DMF/ 140	12	90	22
$Bi(OTf)_3$	DMF/120	24	87	35
PVA@Cu(II) Schiff base complex	H_2O/ R. T.	0.12	98	-[a]

[a] Present work

Because in contrast to the reported catalysts in the literature, which catalyze the preparation of 5-substituted-1*H*-tetrazoles in DMF as a toxic solvent, long reaction times, under high temperatures (>100 °C), PVA@Cu(II) Schiff base complex works in water as a green solvent, very short reaction times and at room temperature. The other notable advantages of this catalyst are: a) its preparation in water, and b) its stability and reusability, so it can be reused five runs without significant reactivity loss.

Conclusion

We have reported preparation of novel heterogeneous recoverable and reusable polyvinyl alcohol immobilized Cu(II) Schiff base complex in water from simple and available reagents, which is able to catalyze green formation of 5-substituted 1*H*-tetrazoles from aldehydes, hydroxylamine hydrochloride and sodium azide at room temperature in short reaction times in water. The catalyst was characterized with FT-IR, UV-Vis, ^{1}H NMR, TGA and ICP instruments. Simplicity, high efficiency and cost effectiveness, easy work-up of the catalyst and the products are among the other notable advantages of this protocol. Various aliphatic and aromatic aldehydes served as suitable substrates for the preparation of substituted tetrazoles with high to excellent yields at room temperature.

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A new polymeric Cu(II) Schiff base complex catalyst is developed, which shows high activities in catalyzing the 5-Substituted 1*H*-Tetrazoles under mild and green conditions.