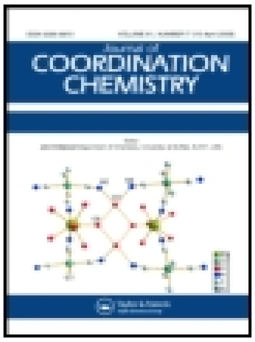

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Zinc(II) complex immobilized on amine functionalized silica gel: A novel, highly efficient and recyclable catalyst for multicomponent click synthesis of 1,4-disubstituted 1,2,3-triazoles

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Zinc(II) complex immobilized on amine functionalized silica gel: A novel, highly efficient and recyclable catalyst for multicomponent click synthesis of 1,4-disubstituted 1,2,3-triazoles

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We report a highly efficient and recyclable heterogeneous zinc catalytic system *via* covalent immobilization of 2-hydroxyacetophenone (2-HAP) onto an amine functionalized silica gel followed by metallation with zinc chloride and its catalytic application in three component click synthesis of 1,4-disubstituted 1,2,3-triazoles. The structure of the synthesized organic-inorganic hybrid material (SiO_2@APTES@2HAP-Zn) has been confirmed by various physico-chemical characterization techniques such as solid-state ^{13}C CPMAS NMR spectroscopy, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction analysis (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, scanning electron microscopy (SEM), atomic absorption spectroscopy (AAS), energy dispersive X-ray fluorescence spectroscopy (ED-XRF), and elemental analysis. The newly designed catalyst works under mild reaction conditions and also exhibits excellent performance in terms of good product yield and high turnover number (TON). One of the most important attributes of the present methodology is that the catalyst can be recycled several times without appreciable loss in its activity as proved by FTIR spectroscopy and SEM analysis. Besides, the heterogeneity test also confirms that no leaching of active catalytic species occurs from the silica supported zinc catalyst which confirms its remarkable structural stability under the reaction conditions.

Keywords: Silica gel; Recyclable catalyst; Click reaction; Triazoles synthesis; Zinc

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1. Introduction

1,2,3-Triazole derivatives represent an important class of heterocyclic compounds that have large scale industrial applications as agrochemicals, photostabilizers, corrosion inhibitors, dyes and optical brightners [1-3]. These motifs also produce large numbers of peptides, oligosaccharides and natural product analogues having exceptional biological properties including anti-HIV, antitumor, anticonvulsant and antimicrobial activities [4, 5]. A few substituted triazoles have been effectively used as deoxyribose nucleic acid cleaving agents and potassium channel activators [6, 7]. Consequently, several methodologies have been developed for the synthesis of 1,2,3-triazole derivatives. However, the well-established methodology is the Huisgen 1,3-dipolar cycloaddition of azides and alkynes which was pioneered by Huisgen in 1967 [8]. Although the Huisgen approach shows high chemoselectivity, it suffers from several limitations such as formation of a mixture of regioisomers, requirement of high temperature and prolonged reaction time, which restricts the scope of its synthetic utility. To circumvent these drawbacks, Sharpless and Meldal introduced the concept of click chemistry wherein a copper based catalyst was used to accelerate the yield of 1,4-disubstituted 1,2,3-triazoles [9, 10]. Later, several other research groups also utilized the click concept for the synthesis of these industrially significant triazole derivatives with slight modifications in the employed reaction conditions [11-14]. Unfortunately, most of these protocols are catalyzed by homogeneous metal complexes which hinder their practical applications and feasibility on a large scale due to metal contamination and recyclability issues. Thus, in order to overcome these difficulties, the fabrication of recoverable and reusable catalysts which combine the best attributes of homogeneous as well heterogeneous catalytic systems is desirable.

Organic-inorganic hybrid catalysts based on solid support materials such as silica, zeolite, alumina, titania, ceria, *etc.* have gained importance because of the increasing worldwide momentum towards the development of environmentally friendly reactions [15-23]. An extensive literature survey reveals that silica gel is an efficient solid support as it is chemically inert, readily available, inexpensive, non-toxic and thermally stable. A large number of organic or organometallic moieties can be robustly anchored on its surface due to the presence of highly reactive silanol groups [24-27]. In this perspective, the grafting of active catalytic species onto silica gel by means of covalent linkage is considered to be the best technique because it minimizes leaching as a consequence of which the catalyst becomes sufficiently robust to survive the harsh reaction conditions.

Thus, in continuation of our ongoing research on the design and synthesis of silica based organic-inorganic hybrid materials and their applications as metal scavengers, sensors, and catalysts for various organic transformations [28-41], herein, we report the fabrication of an efficient and highly recyclable silica supported organic-inorganic hybrid zinc catalyst (SiO_2@APTES@2HAP-Zn) *via* the covalent immobilization of 2-hydroxyacetophenone onto amine functionalized silica followed by metallation with zinc chloride. The resultant heterogeneous zinc catalyst has been applied for synthesis of industrially significant 1,4-disubstituted 1,2,3-triazole derivatives using click chemistry. The results reveal that this catalyst not only exhibits excellent selectivity and activity, but can also be easily recovered from the reaction mixture and reused several times without any appreciable loss in catalytic activity. In addition, excellent product yield, high turnover number, mild reaction conditions, simple work-up procedure and intrinsic stability of the catalyst are features of this protocol that make it indispensable to address industrial prerequisites.

2. Experimental

2.1. *Materials and reagents*

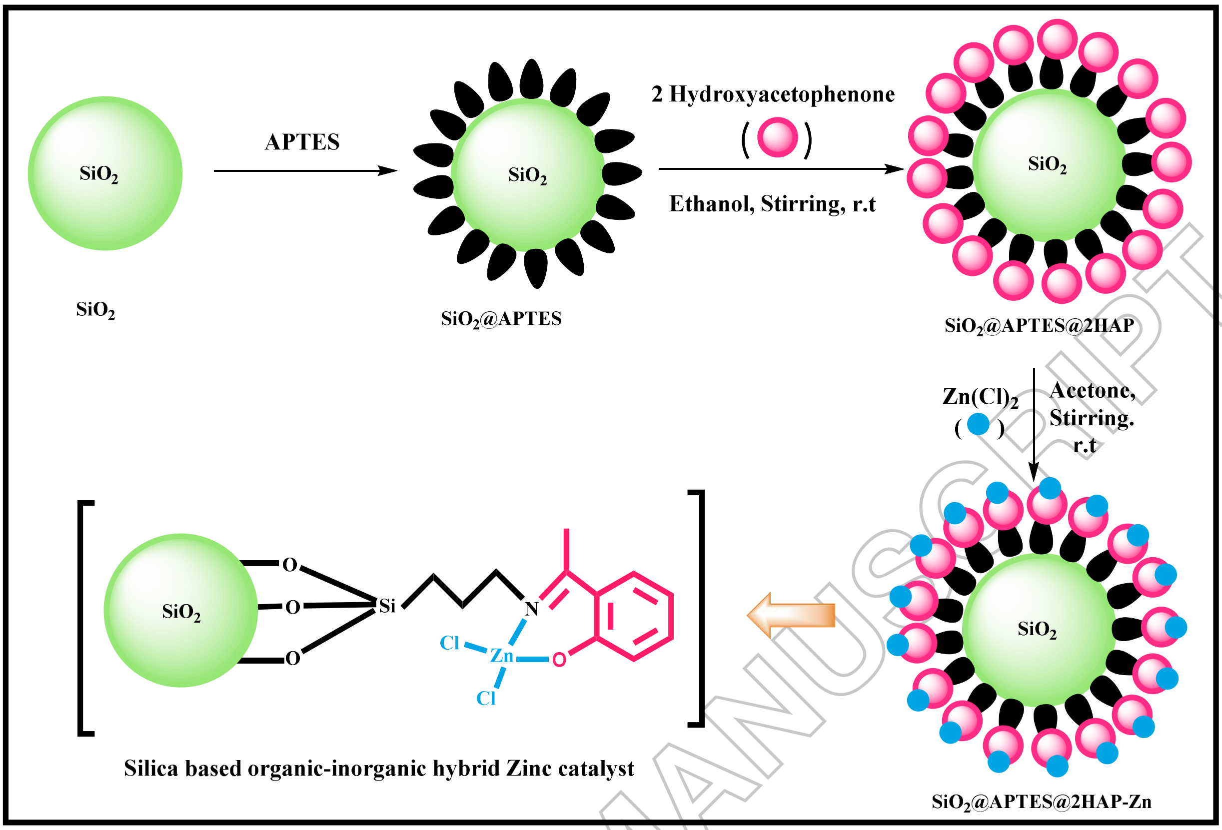
Silica gel (Qualigens), 3-aminopropyltriethoxysilane (APTES) (Fluka), 2-hydroxyacetophenone (Sisco Pvt. Ltd, India) and zinc chloride (Thomas Baker) were commercially obtained and used as received. All other starting materials and reagents used in the reactions were procured from Spectrochem and Alfa Aesar.

2.2. *Physicochemical characterizations*

Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 ADVANCE X-ray diffractometer using graphite monochromated Cu Kα radiation (k = 1.54183 Å) over 2 h range 10-60° at a scan rate of 2 h min^{-1}. Scanning electron microscopy (SEM) images were obtained using a ZEISS EVO 40 instrument. The IR spectra were obtained on a Perkin Elmer Spectrum 2000 FT-IR spectrometer. The BET surface area analysis was carried out using a Gemini-V2.00 instrument (Micromeritics Instrument Corp.) and solid samples were outgassed under vacuum in order to eliminate physisorbed moisture. Elemental analysis (CHN) was performed using an Elementar Analysensysteme GmbH VarioEL V3.00. Solid-state ^{13}C (CPMAS) NMR spectra were recorded on a Bruker DSX-300 NMR spectrometer. Energy dispersive X-ray fluorescence spectroscopy was done on a Fischer scope X-Ray XAN-FAD BC. The amount of zinc content was detected using LABINDIA AA 7000 Atomic Absorption Spectrometer. The triazole products obtained were analyzed and confirmed on Agilent gas chromatography (6850 GC).

2.3. ***Catalyst preparation***

Surface functionalization of silica gel was achieved by suspending 5 g of activated silica gel in 20 mL of 3-aminopropyltriethoxy silane (APTES) using dry toluene as the solvent. The mixture was then refluxed for 10 h in an inert atmosphere with constant stirring [42]. The resultant aminopropyl silica gel (SiO_2@APTES) was filtered, washed thoroughly with toluene, ethanol and acetone, respectively, and dried in a vacuum oven. Thereafter, the silica supported Schiff base ligand (SiO_2@APTES@2-HAP) was synthesized by dispersing SiO_2@APTES and 2-hydroxy acetophenone (2-HAP) in ethanol followed with continuous stirring for 12 h [43]. Finally, the ligand grafted amine functionalized silica support was metallated by adding zinc chloride (scheme 1) to a solution of acetone containing 2 g of SiO_2@APTES@2-HAP to afford the final catalyst (SiO_2@APTES@2-HAP-Zn).



Scheme 1. Synthesis of silica supported organic-inorganic hybrid zinc catalyst (SiO_2@APTES@2HAP-Zn).

2.4. ***Typical procedure for the synthesis of 1,4-disubstituted 1,2,3-triazoles catalyzed using the silica based organic-inorganic hybrid zinc catalyst***

A solution containing alkyne (1.0 mmol), organic halide (1 mmol), sodium azide (1 mmol), 1:1 mixture of water/^{t}BuOH (2 mL) and SiO_2@APTES@2HAP-Zn (20 mg) catalyst was stirred at 55 °C. After completion of the reaction as monitored through Thin-Layer Chromatography (TLC), the catalyst was removed by filtration. The reaction mixture was then extracted with ethyl acetate and dried over anhydrous Na_2SO_4. Finally, the GC-MS analysis of the products was done to confirm the structures of the resultant 1,4-disubstituted 1,2,3-triazole derivatives.

3. Results and discussion

3.1. *Catalyst characterization*

3.1.1. Fourier-transform infrared spectroscopy. Figure 1 shows the FT-IR spectra of SiO_2, SiO_2@APTES, SiO_2@APTES@2HAP and SiO_2@APTES@2HAP-Zn. The FT-IR spectrum of

SiO_2 exhibits strong bands in the low-frequency region (1000-500 cm^{-1}) ascribed to the silica framework such as the Si–O–Si asymmetric stretching band at 1095 cm^{-1} and Si–O symmetric stretching band at 805 cm^{-1}. Additionally, a band at 1649 cm^{-1} is observed in the spectrum due to H-O-H bending vibrations of physically adsorbed water and a broad band centered around 3426 cm^{-1} due to O-H stretching vibrations of hydrogen-bonded surface silanol groups. The surface functionalization of the silica support with the linking agent is confirmed by the appearance of two new peaks at 2928 and 2852 cm^{-1} that are attributed to the CH_2 groups of APTES [44-46]. Finally, for SiO_2@APTES@2HAP-Zn, a strong band at 1626 cm^{-1} due to C=N stretching vibration affirms the Schiff condensation between the NH_2 group and carbonyl group of ligand [47-49]. Further, it should be noted that there is not much difference between the spectra of recovered and fresh catalyst, suggesting that the catalyst is not poisoned during the reaction.

3.1.2. ^{13}C CPMAS NMR spectroscopy. Cross-polarization magic angle spinning ^{13}C nuclear magnetic resonance study is an invaluable tool as it often provides information regarding chemical structure of the organic functional groups present in the hybrid frameworks. Hence, the surface modification of the SiO_2 surface with silane coupling agent has been confirmed using solid state ^{13}C CPMAS NMR spectroscopy. In figure 2, the ^{13}C CPMAS NMR spectrum of SiO_2@APTES is shown. The spectrum exhibits the expected signals at $\delta = 9.3$, 22.3 and 42.9 ppm which can be assigned the three methylene groups (Si–CH_2–, –CH_2– and –N–CH_2–) of the propyl chain of APTES [50]. This validates that the APTES linking agent has been covalently grafted onto the surface of SiO_2.

3.1.3. SEM analysis. Scanning electron microscopy has been utilized to determine the morphology of the synthesized silica based organic-inorganic hybrid materials and the corresponding SEM images are presented in figure 3. The appearance and size of silica gel and the catalyst are very similar. Even the beads of silica gel do not possess any cracks after the surface functionalization during the catalyst preparation. This provides a clear indication that the SiO_2 particles have not been destroyed during the modification reaction, owing to their excellent mechanical stability.

3.1.4. Surface area and elemental analysis. The specific surface areas of the synthesized silica based samples have been calculated using the Brunauer-Emmett-Teller (BET) method and the results are presented in table 1. As expected, the surface area of SiO_2 gets reduced from 232.45 to

155.11 m^2g^{-1} after functionalization of the APTES and it was further reduced to 81.23 m^2g^{-1} upon anchoring the 2-hydroxyacetophenone zinc complex. The reduction in the surface area is due to immobilization of organic moieties onto the porous silica matrix which eventually blocks access of nitrogen gas molecules. This observation directly confirms the successive anchoring of APTES and zinc complex onto the surface of SiO_2. Table 1 also lists the chemical compositions of all the synthesized silica based materials. Increased content of both carbon and nitrogen were detected on moving from SiO_2 to SiO_2@APTES. Further, the elemental analysis data of SiO_2@APTES shows that carbon and nitrogen contents are 5.17% and 1.81%, respectively. Based on these results the C/N ratio has been calculated to be ~2.86 which is close to the theoretical value, thereby confirming incorporation of APTES linking agent into the silica matrix. In addition, the SiO_2@APTES@2HAP-Zn was subjected to AAS analysis after being digested in aqua regia which gives 0.116 mmol of Zn per gram of catalyst. Apart from this, the well-resolved peak of zinc in the ED-XRF spectrum of SiO_2@APTES@2HAP-Zn (figure 4) also provides clear evidence of the immobilization of zinc complex on the modified silica gel.

3.2. *Catalytic performance*

Catalytic performance of silica supported organic-inorganic hybrid zinc complex was evaluated in the one pot synthesis of 1,4-disubstituted triazole derivatives using phenyl acetylene and benzyl bromide as test substrates. To obtain an optimum reaction profile for SiO_2@APTES@2HAP-Zn mediated triazole synthesis, the effect of different reaction parameters such as amount of catalyst, reaction time and temperature, substrate molar ratio and type of solvent have been studied.

3.2.1. Effect of amount of catalyst. In our initial investigations, the efficiency of the click reaction is affected by the amount of SiO_2@APTES@2HAP-Zn and the results are presented in figure 5. Increase in amount of catalyst to 20 mg resulted in enhancement of the conversion percentage of the reactants. A further increase in the catalytic amount beyond this value did not cause considerable increase in the conversion. The optimal amount of SiO_2@APTES@2HAP-Zn was fixed to 20 mg for the rest of the experiments.

3.2.2. Comparison of various catalysts. In order to examine the effect of catalyst on the click synthesis, the model reaction was carried out in the presence of different catalysts. As evident from table 2, the use of simple silica gel failed to render the desired product, thereby showing poor catalytic activity. Use of the homogeneous 2HAP-Zn complex gave higher conversion in comparison to heterogenized SiO_2@APTES@2HAP-Zn catalyst. However, the homogeneous metal catalyst decomposed immediately after the reaction and could not be reused for further catalytic cycles. In particular, SiO_2@APTES@2HAP-Zn system has been fabricated *via* immobilization onto silica gel to acquire the advantages of heterogeneous catalytic system so that it could be easily recovered and reused for several catalytic cycles. In addition, the heterogenized catalyst is devoid of separation problems typically associated with homogeneous catalytic systems.

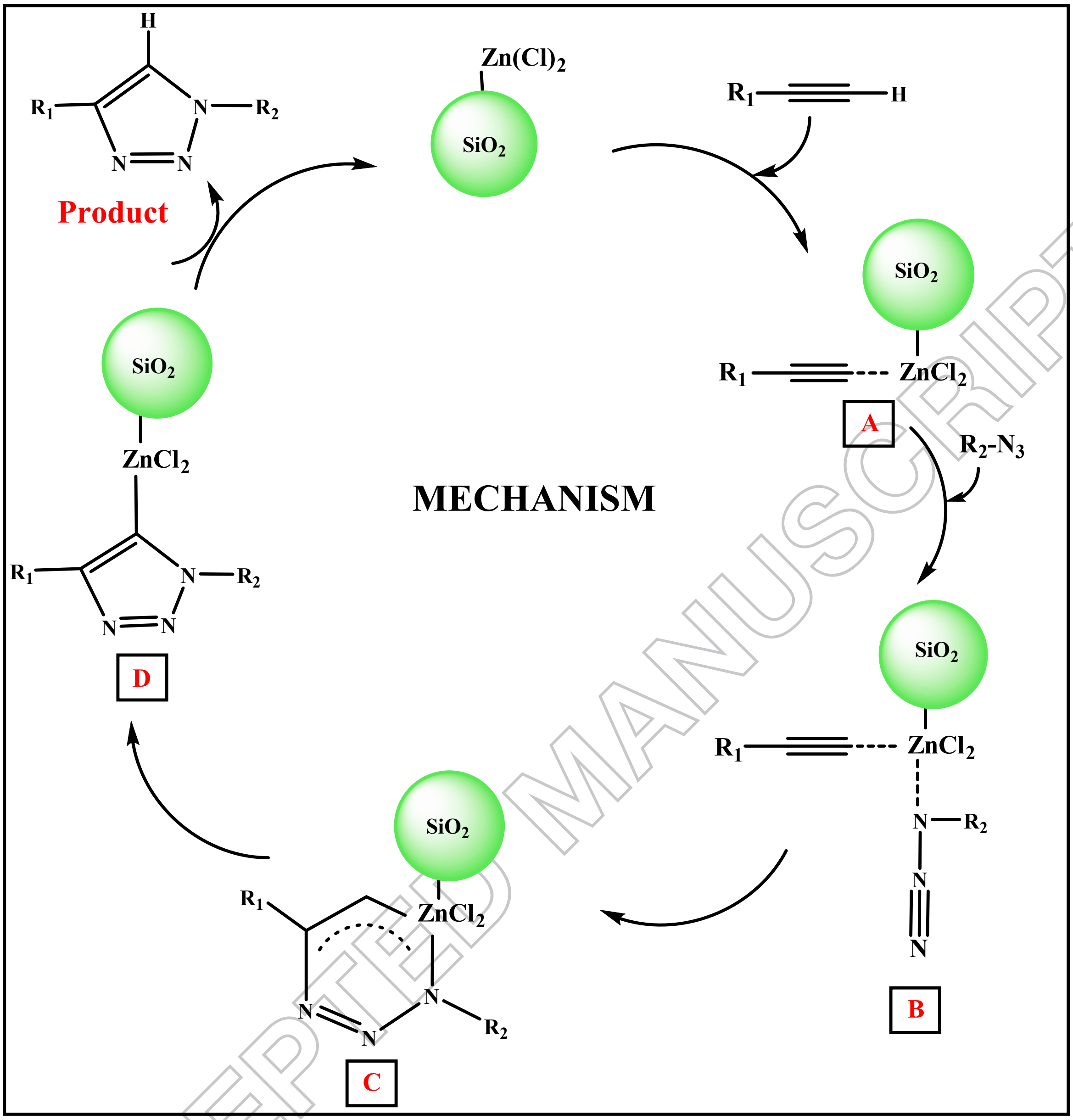
3.2.3. Effect of time and temperature. In order to examine the effect of time and temperature, the model reaction was performed under a diverse range of temperatures (25-65 °C) for different time periods (0.5-2.5 h) and the results are summarized in figure 6. The reaction time had a remarkable influence on the one pot synthesis of triazoles. Detailed examination of the results revealed that a time period of 2 h was appropriate for the maximum conversion of the reactants when the reaction was carried out at 55 °C.

3.2.4. Effect of various solvents. Subsequently, the activity of the silica supported heterogeneous catalyst was evaluated in the click reaction using different solvents in the presence of the model substrates. The effect of solvents on the synthesis of triazole derivatives is illustrated in figure 7. It can be seen that the conversion percentage obtained in these solvents increases in the order acetonitrile < THF < DCM < toluene <ethanol < water < water/^{t}BuOH. Thus, the best catalytic performance was observed when a 1:1 mixture of water/^{t}BuOH was employed as solvent.

3.2.5. Effect of substrate molar ratio. Having established 1:1 mixture of water/^{t}BuOH as the best solvent for the click reaction, we then investigated the influence of substrate ratio and the results are summarized in figure 8. Different molar ratios of phenyl acetylene, benzyl bromide and sodium azide (1:0.5:0.5, 1:1:1 and 1:2:2) were considered while keeping the other parameters fixed. Upon utilizing 1:0.5:0.5 substrate ratio, a moderate conversion was observed. When equal molar ratio of all three substrates was applied, the reaction time was shortened and maximum conversion was observed. Hence, 1:1:1 molar ratio was the minimum requirement for the effective one pot synthesis of triazoles. It was also noticed that further increase in the molar ratio did not have much effect on the conversion percentage.

3.2.6. Scope and versatility of the protocol. To further explore the potential of this catalyst for 1,4-disubstituted 1,2,3-triazole synthesis, a series of terminal alkynes and organic halides were subjected to the click reaction under the optimized reaction conditions using SiO_2@APTES@2HAP-Zn (table 3). Analysis of the results showed that most of the substrates produced the expected triazole products with good to excellent conversion, indicating remarkable catalytic efficacy of the silica based zinc catalyst. For example, phenyl acetylene was almost quantitatively converted to the desired product. The most important attributes of the present methodology are that the click reaction is devoid of unwanted products and the catalyst can be recycled for six consecutive cycles without appreciable loss in its performance.

3.2.7. Mechanism. A probable reaction mechanism for the synthesis of 1,4-disubstituted 1,2,3-triazoles catalyzed by the silica based organic-inorganic hybrid zinc catalyst has been proposed and illustrated in scheme 2. Initially, zinc coordinated acetylide complex is generated in step I via the interaction of zinc catalyst and terminal alkyne species. The complex thus formed reacts with azide to produce complex B which gets transformed into triazolide intermediate C. This triazolide intermediate produces heterocyclic complex D which subsequently undergoes protonolysis, delivering the desired product and regenerating the active catalyst [51, 52].

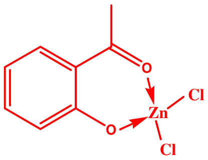


Scheme 2. Proposed mechanism for synthesis of 1,4-disubstituted 1,2,3-triazoles.

3.2.8. Hot Filtration test. A hot-filtration test was performed using the model substrates in order to test the heterogeneous nature of the newly fabricated catalyst. At about half the reaction time, the solid catalyst was separated from the reaction mixture through filtration and the conversion percentage obtained after GC-MS analysis of the resultant supernatant was found to be 67%. Thereafter, the supernatant was subjected to further heating under the same reaction conditions. No increment in the conversion of the reactants was observed. This supported the observation that the active metal species did not leach from the solid catalyst. Further, the atomic absorption spectrometric analysis of the filtrate also confirmed the absence of metal in the reaction mixture. These studies clearly demonstrated that the zinc(II) complex was intact with the support, confirming the true heterogeneous nature of the catalyst. Complexes of 2-hydroxyacetophenone with metals such as Cu(II), Ni(II), Co(II) and Zn(II) exhibit remarkable stability as evident from the literature [53]. In fact, the binding constant value of the 1:1 metal complex of 2-hydroxyphenone with Zn(II) has been found to be 6.30 using Calvin Bjerrum titration technique as modified by Irving and Rossotti.

Equation used: $\log \mathrm{K} = \mathrm{pL} + \log\,[\bar{\mathrm{n}}/(1-\bar{\mathrm{n}})]$

The structure of 2HAP-Zn complex is as follows:



3.2.9. Catalyst recycling test. One of the main reasons for immobilizing homogeneous metal complexes onto solid supports is to enhance the lifetime of the resultant catalyst, thereby rendering it suitable for industrial applications. In order to investigate the reusability of the SiO_2@APTES@2HAP-Zn catalyst, the model reaction was performed under the optimized reaction conditions. Upon completion of the reaction, the catalyst was separated by filtration after each run, dried under vacuum and then subjected to the next reaction cycle under the same conditions. It is evident from figure 9 that there was no significant decrease in conversion percentage even after six runs, indicating excellent durability and reusability of the catalyst. SEM analysis of the reused catalyst after the sixth run (figure 3(c)) showed no significant difference in the SEM images of the fresh and the reused catalyst which provided evidence for the good structural stability of SiO_2@APTES@2HAP-Zn under the employed reaction conditions.

3.2.10. Comparison with the literature precedents. The efficiency of the silica based organic-inorganic hybrid catalyst (SiO_2@APTES@2HAP-Zn) was compared with the previously reported catalytic system for the synthesis of triazole derivatives. From table 4, it is evident that the newly fabricated zinc catalyst is far more proficient in terms of product yield and cost. Besides, the SiO_2@APTES@2HAP-Zn can be easily recovered through simple analytical techniques such as filtration or centrifugation, and reused for six consecutive cycles without any significant loss in its activity making it an interesting alternative for zinc catalyzed click promoted triazole synthesis.

4. Conclusion

We have developed a silica based organic-inorganic hybrid zinc catalyst (SiO_2@APTES@2HAP-Zn) with good activity and recyclability through the covalent immobilization of 2-hydroxyacetophenone on the surface of the amine functionalized silica support followed by its metallation with zinc chloride. The resultant heterogeneous catalytic system exhibits remarkable efficiency in terms of product yield and high turnover number in the synthesis of 1,4-disubstituted 1,2,3-triazole derivatives. The hot filtration test ensures that the catalyst works in a heterogeneous manner and is devoid of leaching problem. The facile recovery, coupled with the intrinsic stability of the support material, allows the catalyst to be recycled six times without any discernible loss in its activity. Simple work-up procedure, mild reaction condtions and cost effectiveness are additional attributes of the present protocol that render it suitable for addressing various economic and industrial concerns.

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Table 1. Physico-chemical parameters of SiO_2, SiO_2@APTES and SiO_2@APTES@2HAP-Zn.

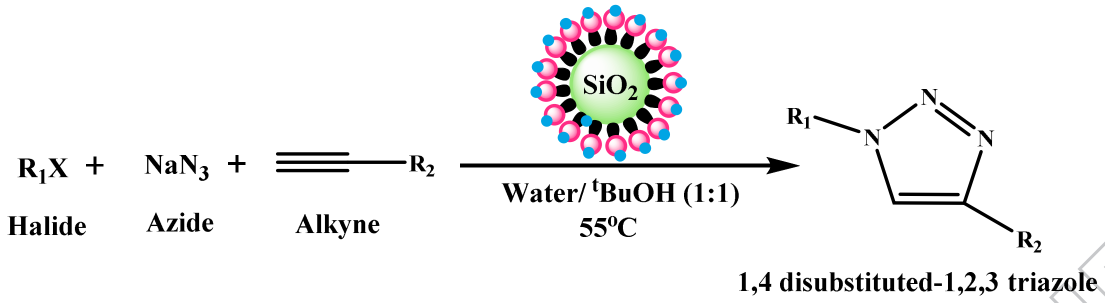
Material	Elemental analysis			BET surface area (m^2g^{-1})
	C(%)	H(%)	N(%)	
SiO_2	-	-	-	232.54
SiO_2@APTES	5.17	1.26	1.81	155.11
SiO_2@APTES@2HAP-Zn	14.94	2.59	3.51	81.23

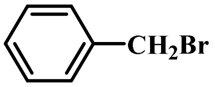
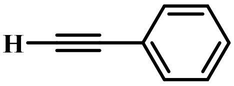
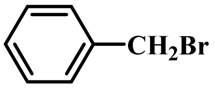
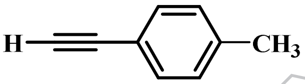
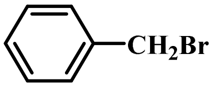
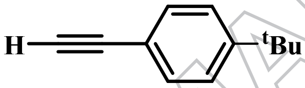
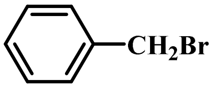
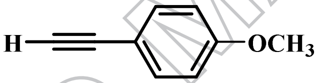
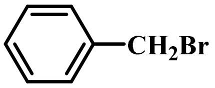
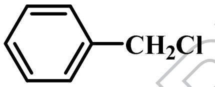
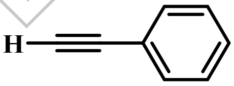
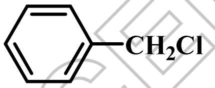
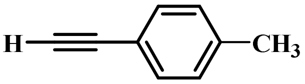
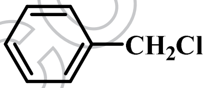
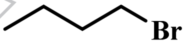
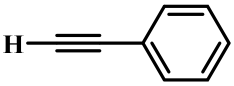
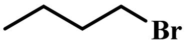
Table 2. Model reaction performed using various catalysts.[a]

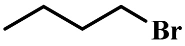
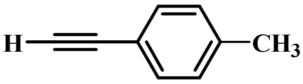
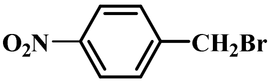
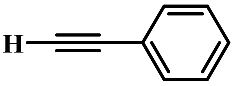
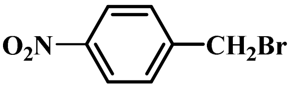
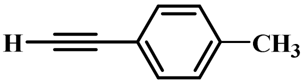
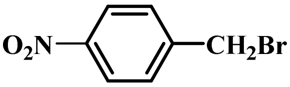
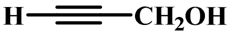
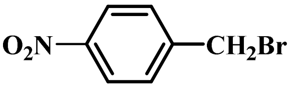
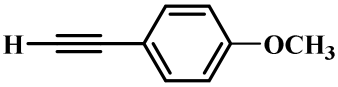
Entry	Catalyst	Conversion (%)[b]	TON[c]
1	SiO_2	-	-
2	2HAP-Zn[d]	97	418
3	SiO_2@APTES@2HAP-Zn	95	409

[a] Reaction conditions: phenyl acetylene (1 mmol), benzyl bromide (1 mmol) and sodium azide (1 mmol), 1:1 mixture of Water/^{t}BuOH (2 mL), catalyst (20 mg) stirring at 55 °C. [b] Conversion was determined by GC-MS. [c] TON is the number of moles of product per mol of catalyst and TOF = TON per hour. [d] 0.0023 mmol.

Table 3. SiO_2@APTES@2HAP-Zn catalyzed one pot synthesis of 1,4-disubstituted 1,2,3-triazoles.

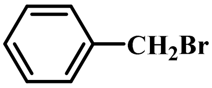
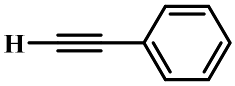
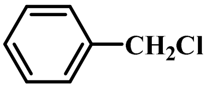
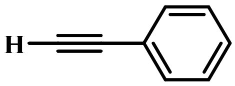
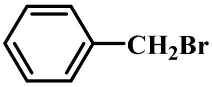
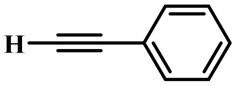
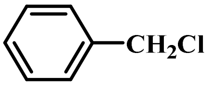
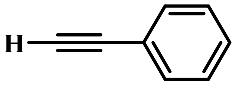
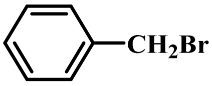
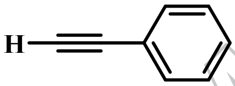
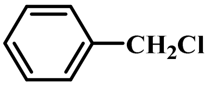


Entry	Halide	Alkyne	Time (h)	Conversion[b] (%)	TON[c]
1.			2	95	409
2.			2	96	414
3.			2.5	90	388
4.			2	92	397
5.		$H-\equiv-(CH_2)_3CH_3$	3	88	379
6.			1.5	94	405
7.			2	96	413
8.		$H-\equiv-(CH_2)_3CH_3$	2.5	91	392
9.			2	85	366
10.		$H-\equiv-CH_2OH$	3	90	388

11.			3	91	392
12.			2.5	86	371
13.			3	88	379
14.			3.5	80	345
15.			3.5	82	353

[a] Reaction conditions: terminal acetylene (1 mmol), organic halides (1 mmol) and sodium azide (1 mmol), catalyst (20 mg), water/^{t}BuOH (2 mL), stirring at 55 °C. [b] Conversion (%) was determined using GC-MS. [c] TON is the number of moles of product per mol of catalyst.

Table 4. Comparison of the catalytic activity of SiO_2@APTES@2HAP-Zn catalyst with some recently reported zinc catalysts for the synthesis of 1,4-disubstituted 1,2,3-triazoles.

Entry	Organic halides	Terminal alkynes	Catalytic conditions	Yield (%)	Reference
1.			zinc(II) L-prolinate (2 mol %), water reflux, 2 h	91	[14]
2.			zinc(II) L-prolinate (2 mol %), water reflux, 2 h	91	[14]
3.			Zn/C (10 mol %), DMF, 50 °C, 15 h	81	[13]
4.			Zn/C (10 mol %), DMF, 50 °C, 15 h	76	[13]
5.			SiO_2@APTES@2HAP-Zn, water/^{t}BuOH, 55 °C	93	Present study
6.			SiO_2@APTES@2HAP-Zn, water/^{t}BuOH, 55 °C	92	Present study

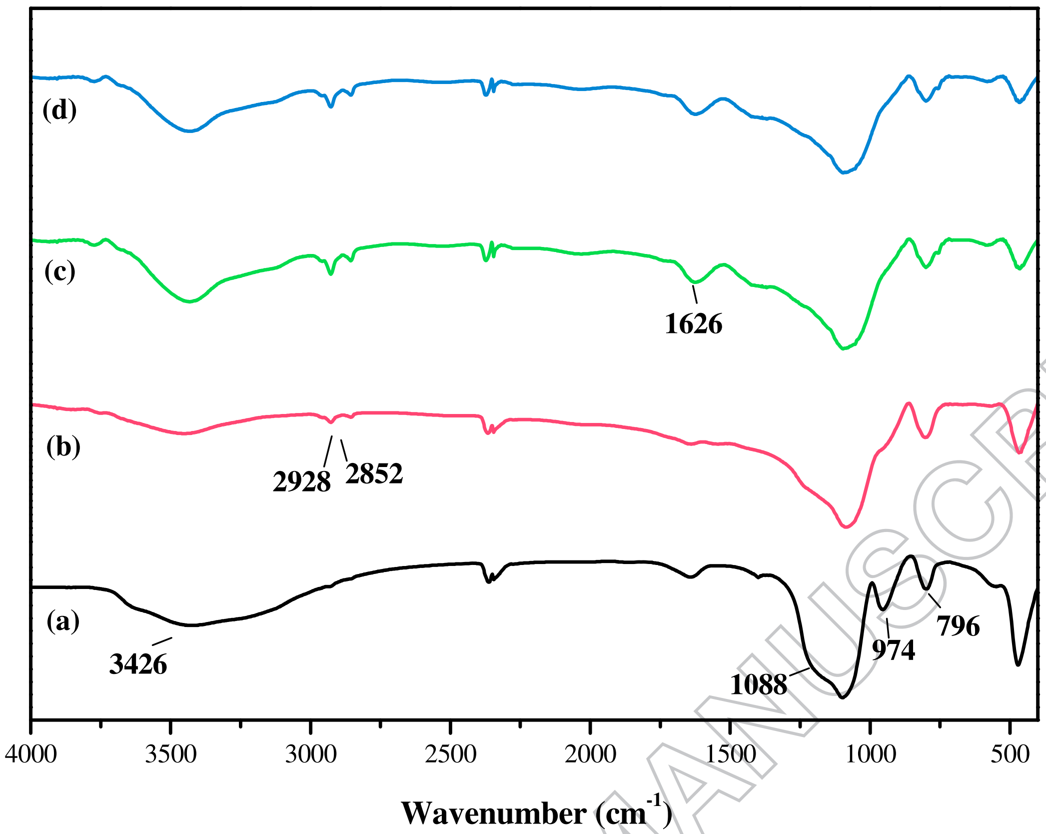


Figure 1. FT-IR spectra of (a) SiO_2, (b) SiO_2@APTES, (c) SiO_2@APTES@2HAP-Zn, (d) recovered SiO_2@APTES@2HAP-Zn.

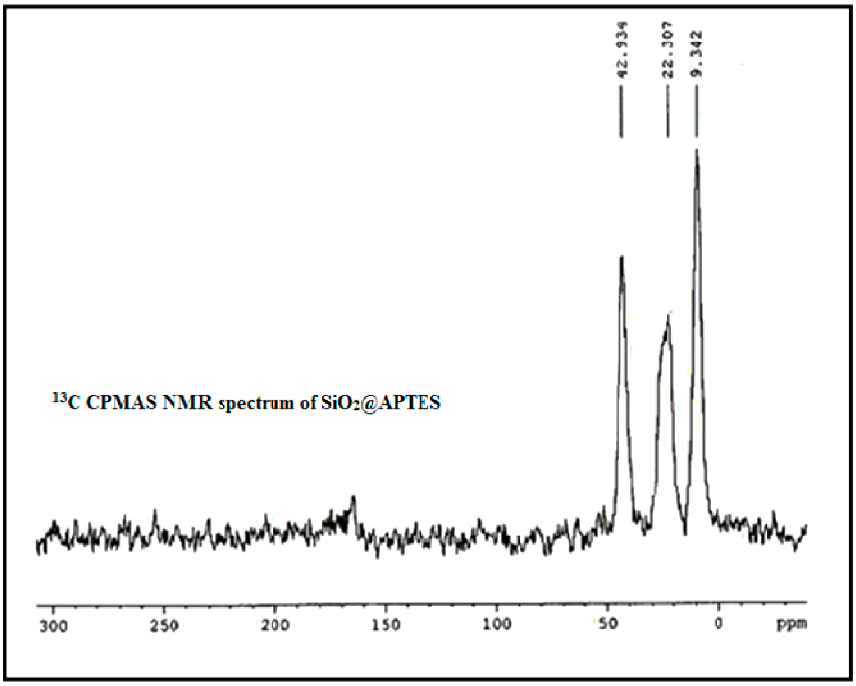


Figure 2. ^{13}C CPMAS NMR spectrum of SiO_2@APTES.

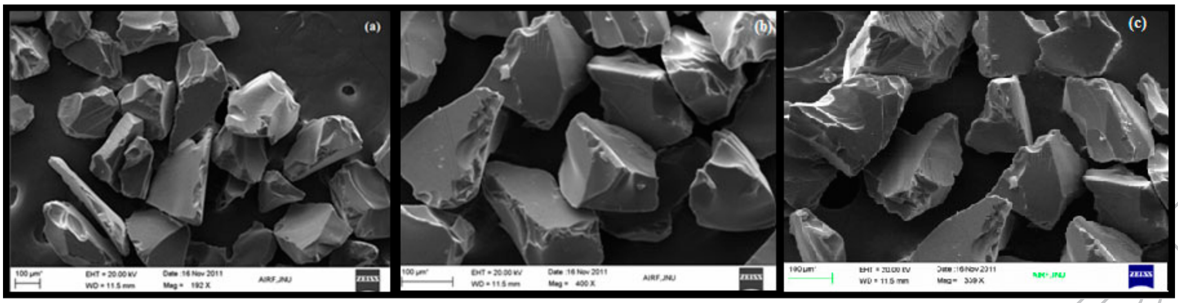
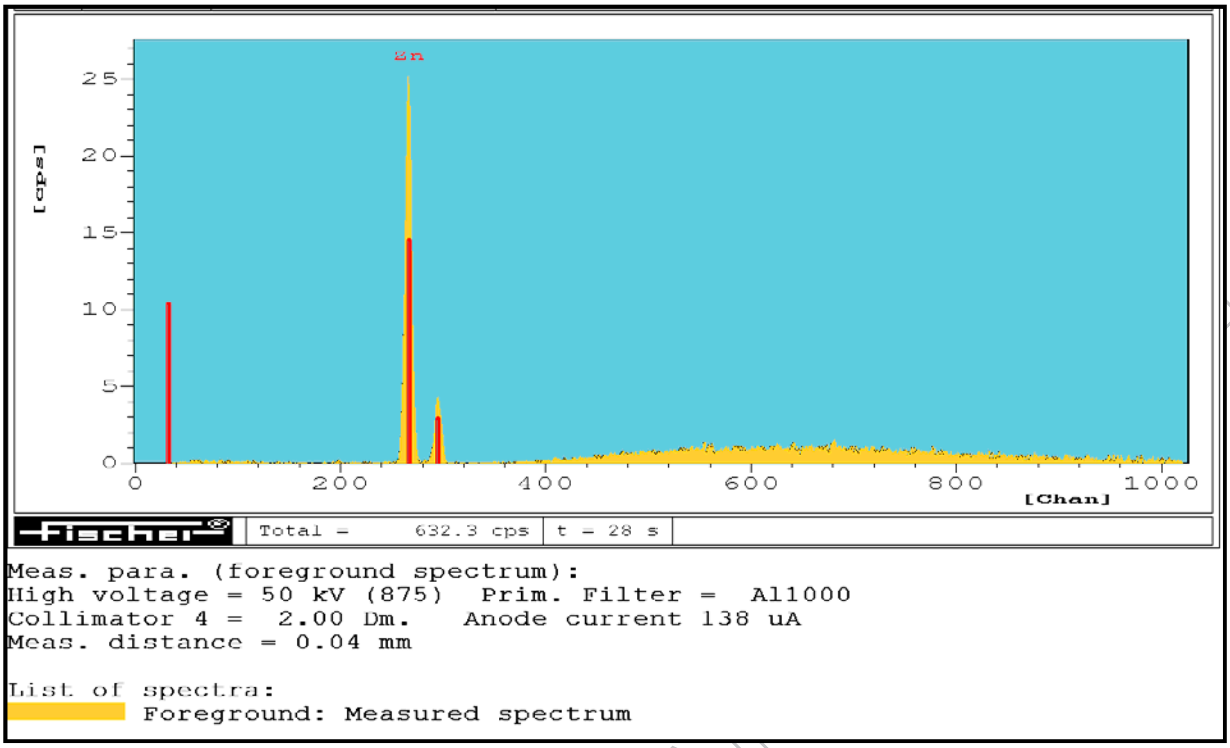


Figure 3. SEM images of (a) silica gel, (b) SiO_2@APTES@2HAP-Zn catalyst, (c) recovered SiO_2@APTES@2HAP-Zn catalyst.



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Total =        632.3 cps   t = 28 s
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)  Prim. Filter =  Al1000
Collimator 4 =  2.00 Dm.   Anode current 138 uA
Meas. distance = 0.04 mm

List of spectra:
          Foreground: Measured spectrum
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Figure 4. ED-XRF spectrum of SiO_2@APTES@2HAP-Zn catalyst.

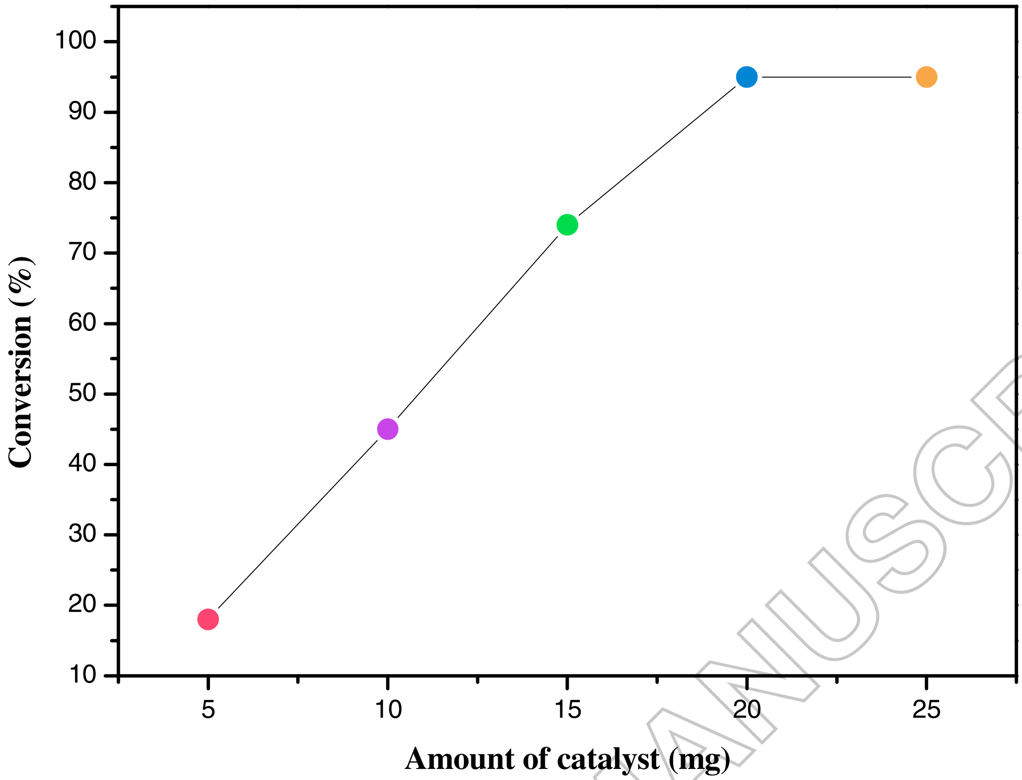


Figure 5. Effect of amount of catalyst on the model reaction (reaction conditions: phenyl acetylene (1 mmol), benzyl bromide (1 mmol) and sodium azide (1 mmol), 1:1 mixture of water/^{t}BuOH (2 mL), catalyst, stirring at 55 °C).

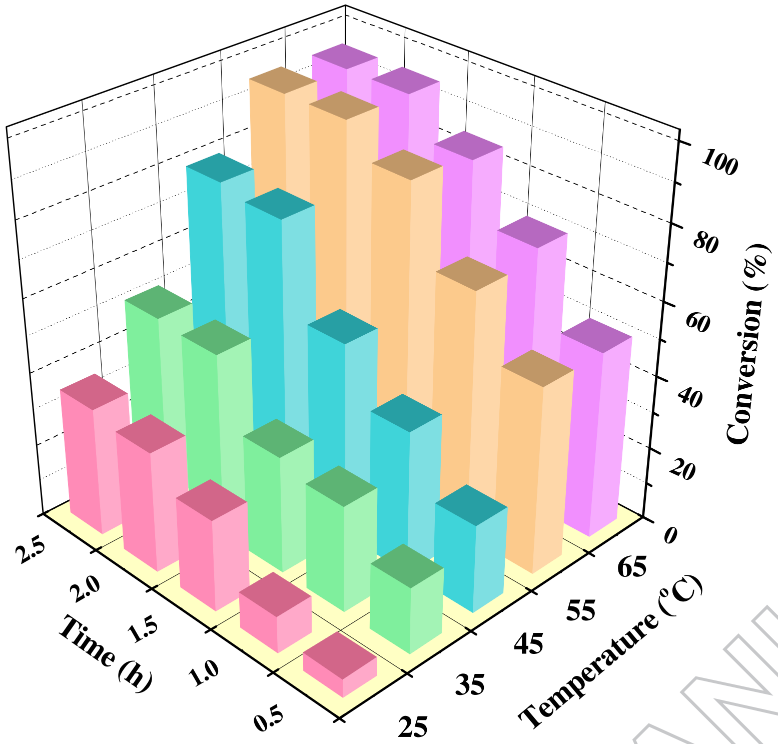


Figure 6. Effect of time and temperature on the model reaction (reaction conditions: phenyl acetylene (1 mmol), benzyl bromide (1 mmol) and sodium azide (1 mmol), 1:1 mixture of water/^{t}BuOH (2 mL), catalyst (20 mg), stirring).

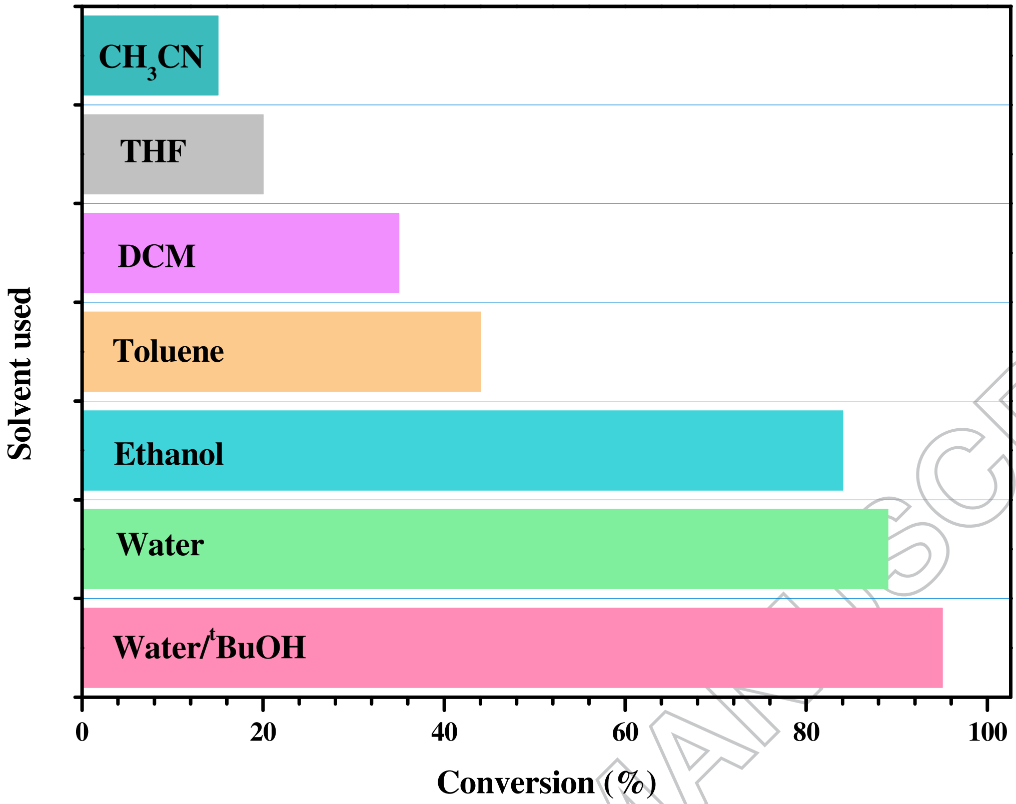


Figure 7. Effect of solvent on the model reaction (reaction conditions: phenyl acetylene (1 mmol), benzyl bromide (1 mmol) and sodium azide (1 mmol), catalyst (20 mg), solvent (2 mL), stirring at 55 °C).

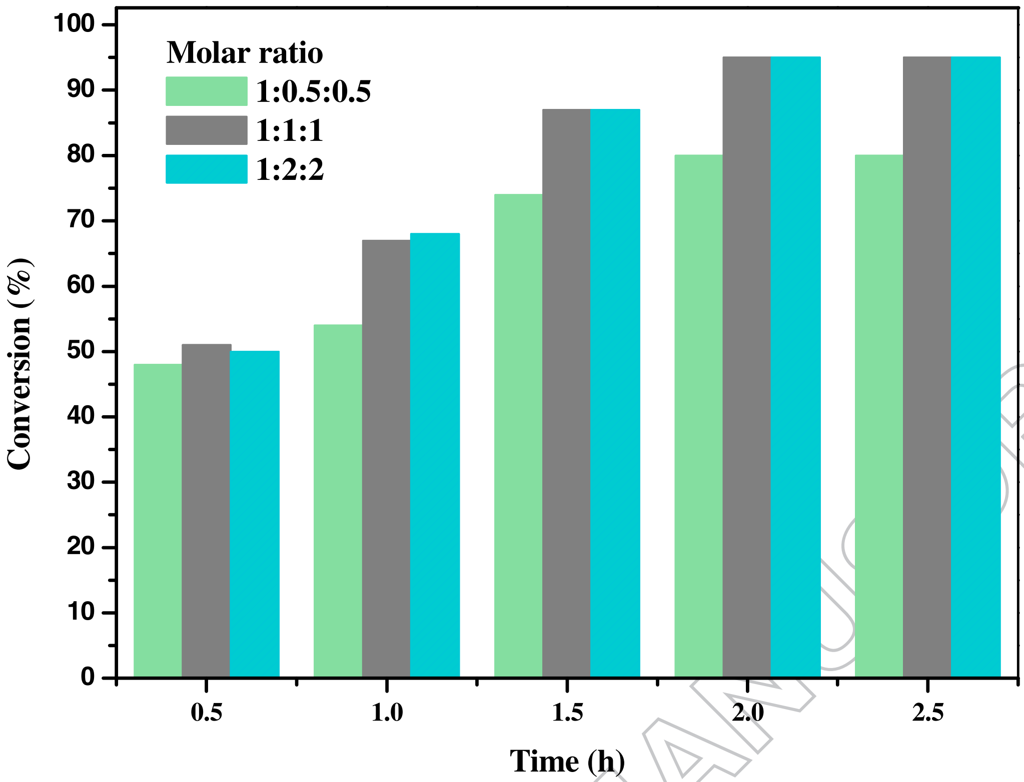


Figure 8. Effect of substrate molar ratio on the model reaction (reaction conditions: phenyl acetylene (1 mmol), benzyl bromide (1 mmol) and sodium azide (1 mmol), catalyst (20 mg), water/^{t}BuOH (2 mL), stirring at 55 °C).

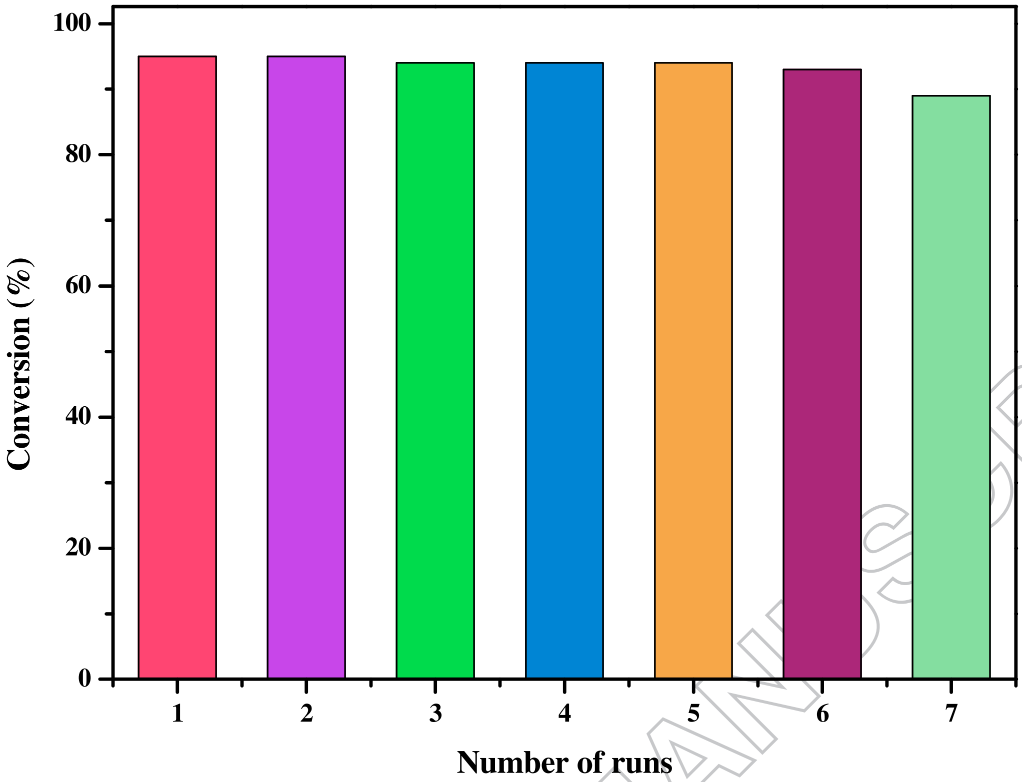
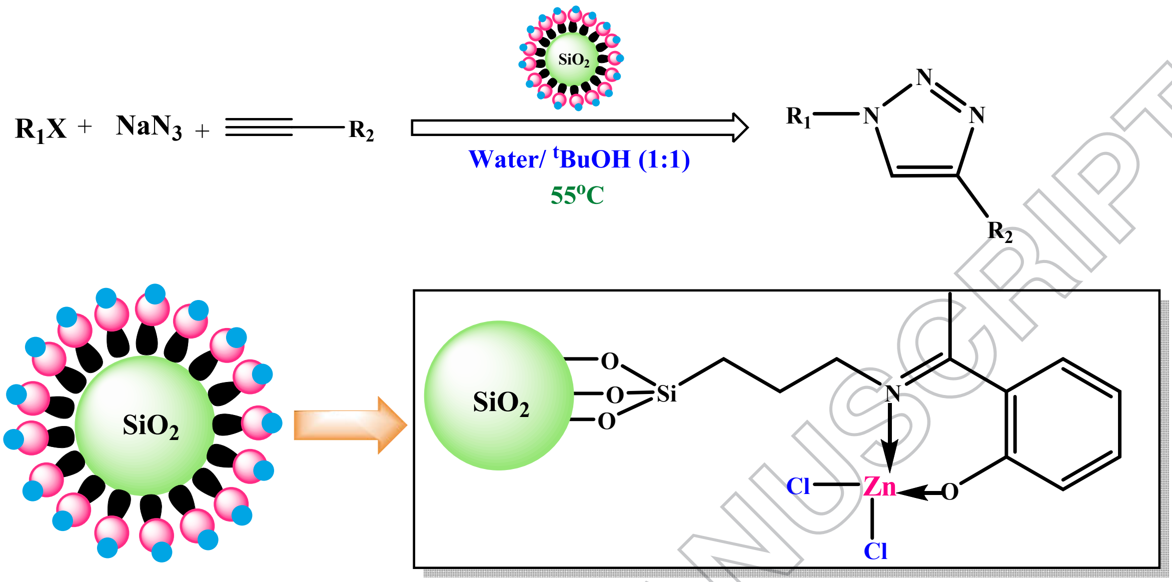


Figure 9. Catalytic recyclability test for multicomponent click synthesis of 1,2,3-triazoles (reaction conditions: phenyl acetylene (1 mmol), benzyl bromide (1 mmol) and sodium azide (1 mmol), 1:1 mixture of water/^{t}BuOH (2 mL), catalyst (20 mg) stirring at 55 °C).

Graphical abstract



Silica based organic-inorganic hybrid zinc catalyst

Excellent product yield *High Turnover number* *Ease of catalyst separation*

Recyclable & reusable catalyst *Mild reaction conditions* *Simple workup procedure*