

## Cu (I) nanoparticles immobilized onto Poly (Vinylpyridine-*N-N*-Methylenebisacrylamide-Acrylicacid) as a new, efficient and recyclable catalyst for the regioselective synthesis of 1, 2, 3-Triazoles *via* click reaction in water

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### Abstract

Poly(vinylpyridine-*N-N*-methylenebisacrylamide-acrylicacid) (2-VP-MBAm-AA) was prepared from the reaction of TiO<sub>2</sub>-methacryloxypropyltrimethoxysilane (TiO<sub>2</sub>-MAPTMS) with 2-vinylpyridine, methylenbisacrylamide (MBAm) and tert-butyl acrylate (*t*-BuA). Subsequently (2-VP-MBAm-AA) was reacted with CuI to give the Cu(I) NPs supported onto the above polymer. These immobilized nano-particles were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), FT-IR and inductively coupled plasma optical emission spectrometry (ICP-OES). This well characterized composite was examined as effective and reusable heterogeneous catalyst in water for the regioselective synthesis of 1,4-disubstituted 1,2,3-triazoles in excellent yields. The catalyst can be recovered by simple filtration and reused for at least five runs *without* losing its efficiency.

**Keywords:** 1, 2, 3-Triazoles; Click Reaction; Cu(I) Nanoparticles; Heterogeneous Catalysis; Regioselective.

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## INTRODUCTION

Nowadays research in synthetic organic and medicinal chemistry, are focused on the synthesis of structurally complex molecules through a rational design. Importantly, if these molecules show any practical applications, the synthetic pathway should be both synthetically operational and economically feasible [1].

Due to their high accessible surface area and unique quantum effect, immobilized-metal nanoparticles are among the very interesting and effective catalytic components [2]. Among different base-metal-NPs, copper nanoparticles (Cu NPs) show the particularly unique catalytic activity in a broad range of chemical transformation and energy related areas such as the Huisegn 1,3-dipolar cycloaddition of azide-alkyne [3, 4], hydrogenation [5], reduction

[6, 7], oxidation [8] and cross-coupling reactions [9].

Utilization of metal-NPs in catalyzed organic transformations have attracted much attention of organic synthetic chemists due to their remarkable electronic, optical, and catalytic qualities and also their significant large surface area to volume ratio [10, 11].

Cu(I) and Cu(II)-catalyzed reactions in organic transformations are well-studied and appreciated [12]. Based on the substantial kind of surface, size and quantum effects, use of nanoparticles (NPs), with the well-recognized unique properties are more favorable comparing with the use of their ordinary counter parts [13]. NPs are more active under mild reaction conditions and at the same time the essential features of a heterogeneous catalysis are maintained [13].

In addition, the industrial catalysts often work

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on the surface of metals, thus metal-NPs, which has much surface area per unit volume or weight in comparison with virgin metal are considered as gifted catalysts [14].

Copper NPs can be provided *via* different procedures such as thermal decomposition of precursors, reduction from a solution by mild reducing agents as well as electrochemical methods [12, 15-19].

They can also be prepared by photoreduction, MWI, micro emulsion techniques and laser ablation [20-25]. In addition, using ultrasonic irradiation recently has attracted tremendous attention in the preparation of nanomaterials [26-28].

Cu-based nanocatalysts have exhibited several applications in the field of nanoscience and nanotechnology, including a wide range of catalyzed-organic reactions, electrocatalysis, and photocatalysis [29-37].

Immobilization of homogeneous catalysts on solid supports often presents advantages. These supported catalysts have attracted much attention in organic synthesis for different reasons [38, 39] including easy separation from the reaction mixture by simple filtration and sometimes providing high catalytic activity, stability, and selectivity in comparison to unsupported materials [40, 41].

The cycloaddition is the reaction of a dipolarophile with a 1,3-dipolar compound that leads to 5-membered heterocycles. The azide-alkyne Huisgen cycloaddition is a 1,3-dipolar cycloaddition between an azide and a terminal or internal alkyne to give 1,2,3-triazole ring. Rolf Huisgen was the first who understood the scope of this organic reaction. Regrettably, the thermal Huisgen 1,3-dipolar cycloaddition of alkynes to azides required elevated temperatures and often produced mixtures of the two regioisomers when asymmetric alkynes are used [42]. In this respect, the classic 1,3-dipolar cycloaddition fails as an ideal reaction as well as requiring harsh reaction conditions [43].

However, the Cu(I)-catalyzed 1,3-dipolar Huisgen cycloaddition has circumvented these back draws.

In 2002, Sharpless *et al.* [44] reported that the use of catalytic amounts of Cu(I) resulted in the rapid and regioselective Huisgen azide-alkyne cycloadditions at ambient temperature. Latter they called this reaction as a cream crop of click reaction [45-47].

The role of Cu(I) as a coordinating agent in the mechanistic pathway of click reactions has now

been well established. As a matter of fact the coordination of Cu(I) with terminal alkynes along with the activation of azide species to produce a copper-azide-acetylide complex were responsible for such advantages [48, 49]. Nowadays, it is well known that the ligand protects the Cu ion from undesired interactions leading to degradation and generation of side products and more importantly prevents the oxidation of the Cu(I) species to the Cu(II) [50, 51]. Moreover, immobilization of Cu(I) nanoparticles on different kinds of supports compared to Cu(0) NPs is a useful method to make them heterogeneous, thus easily recoverable and reusable [52-54].

Thus, notable variant of the Huisgen 1,3-dipolar cycloaddition is the modified Cu(I)-catalyzed reaction is no longer a true concerted cycloaddition, in which organic azides and terminal alkynes are united to afford 1,4-regioisomers of 1,2,3-triazoles as the sole products.

The copper(I)-catalyzed variant was first reported in 2002 in independently Meldal at the Carlsberg Laboratory in Denmark [55] and then by K. Barry Sharpless at the Scripps Research Institute [47]. Thus, at ambient and green conditions, 1,2,3-triazoles can be synthesized. They are a significant class of heterocyclic compound due to their usefulness as agrochemicals, dyes, corrosion inhibitors, photostabilizers, fluorescent whiteners and optical brightening agents [56] and photographic materials [57-61].

1,2,3-Triazoles exhibit a wide range of biological activity and even pharmaceutical properties such as antiviral, antifungal, antitubercular [62], antiepileptic antimalarial, antidiabetic, anticancer [63], antibacterial, antiallergic, anti-HIV activity and selective  $\beta_3$  adrenergic receptor agonist [64-68].

Nowadays, it has been found that *N*-substituted 1,2,3-triazoles have more potential uses than simple 1,2,3-triazole derivatives [69]. Nonetheless, for the synthesis of *N*-substituted 1,2,3-triazoles *via* Cu(I)-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC) [70], the starting materials, such as functional alkynes and organic azides were not easily accessible and those commercially available are expensive.

In addition, although the synthesis of *N*-substituted 1,2,3-triazoles proceed smoothly in the presence of Cu salts as homogeneous catalyst, their separation and recovery from the reaction mixture is usually difficult. Besides, it is possible that the obtained 1,2,3-triazoles were contaminated by

the Cu metal in homogeneous catalysis. In order to overcome the above deficiencies and cumbersome, immobilizing the Cu salts as heterogeneous catalysts in CuAAC reaction is still in much demands.

Recently, polymer-supported reagents have attracted much attention as insoluble matrices in organic synthesis [71]. A wide range of polymer-supported nanoparticles of Cu(I) as reusable catalyst in the click synthesis of 1,2,3-triazoles between azides and alkynes have been reported [72-74]. Polymeric supports bearing nitrogen as electron releasing atoms are of distinctive importance. One of such polymers is cross-linked. Poly(vinylpyridine) (PVPy) which is a functionalized polymer is able to coordinate with different transition metal ions. The complexation between PVPy and several transition metals have been prepared and employed as catalysts in several organic transformations [75-80].

Cross-linked PVPy, as insoluble polymer showing unique properties, nowadays they are frequently used as support for preparing heterogeneous catalysts. It shows extraordinary properties such as: (a) it can undergo easy functionalization, (b) it has several accessible functional groups, (c) it is not hygroscopic, (d) it can be provided easily and even some of them are commercially available, (e) it can be easily filtered, and (f) it can be swelled in conventional organic solvents [81]. Noticeably, PVPy has two market purchasable isomers so-called poly(4-vinylpyridine) ( $P_4$ VPy), and poly(2-vinylpyridine) ( $P_2$ VPy) [81]. Some differences in the performance and properties between some derivatives of  $P_4$ VPy and  $P_2$ VPy have been recognized and previously reported [82-86].  $P_2$ VPy can be made with different strategies exhibiting fascinating physical and chemical properties [81].

Poly (2-VP-MBAm-AA) is a copolymer that has been prepared from 2-vinyl pyridine and tert-butyl acrylate (*t*-BuA) as a monomer and *N,N*-methylenebisacrylamide (MBAm) as a crosslinker to acquire a three-dimensional skeleton [83].

We are interested in heterocyclic chemistry [87-95] *via* MCR [73, 74, 96, 97] under green conditions [98] and heterogeneous catalysis, applied in a wide range of organic transformations [99]. We have also recently had successful attempts for the synthesis of 1,2,3-triazoles, *via* click reaction under heterogeneous catalysis [73-75, 100-104] including their theoretical studies.

Worthy to emphasize that the Poly (2-VP-MBAm-AA) nanocomposite has never been examined as

catalyst in organic transformation but used as a colorimetric sensor based on dithizone-anchored poly (vinyl pyridine-*N,N*-methylenebisacrylamide-acrylic acid) (poly (2-VP-MBAm-AA)) nanocomposite for detection of mercury and lead ions trace levels from aqueous media [83].

In this study, we have investigated the reaction of  $TiO_2$ -MAPTMS with 2-vinylpyridine, methylenbisacrylamide and tert-butyl acrylate to obtain the poly (vinyl pyridine-*N,N*-methylenebisacrylamide-acrylic acid) (poly (2-VP-MBAm-AA)) [83] and used it as a support of immobilization of nano-Cu(I) for the preparation of a novel heterogeneous catalyst so called  $TiO_2$ /poly (2-VP-MBAm-AA)-CuI.

For preventing the agglomeration tendency of NPs, Cu(I) NPs were prepared *in situ* [102] and supported on the polymer surface to afford the immobilized heterogeneous catalyst. This novel nanocatalyst was examined in a one-pot three-component click synthesis of 1,4-disubstituted-1*H*-1,2,3-triazoles involving  $\alpha$ -haloketones or benzyl halides, sodium azide, and terminal alkynes *via* click reaction in water as a greenest and most abundant solvent.

Thoroughly Cu-NPs were prepared *via* a facile and effective methodology. By using the above-mentioned novel catalyst, the regioselective products could be separated by a simple filtration, thus, avoiding time-consuming and problematic separation steps. High yields, short reaction times, regioselectivity, mild reaction conditions and five repeated runs, with very low leaching of the immobilized catalyst, make this strategy very simple and useful for the synthesis of wide range of 1,4-disubstituted 1,2,3-triazoles.

Furthermore, using water as green reaction medium and experimental simplicity are other advantages of using this catalyst in the synthesis of triazoles *via* click reaction.

CuI nanoparticles has less cytotoxicity of the traditional Cu(I) reagents. Hence, we think our catalyst is worthwhile to be examined to other copper-catalyzed organic transformations.

## EXPERIMENTAL

### Materials and methods

*N,N*-Dimethylformamide (DMF) and acetonitrile were distilled and stored over 4 Å molecular sieve before use; other reagents were used as received from Aldrich and Merck Chemical Companies with high-grade quality. Copper content was measured

by SPECTRO ARCOS ICP-OES analyzer. Scanning electron micrographs were recorded using Tescan Vega-3 LMU SEM instruments. FT-IR spectra were recorded on FT-IR Bruker Tensor 27 instrument using KBr disks in the 500–4,000  $\text{cm}^{-1}$  region.

#### Preparation of the $\text{TiO}_2$ /poly (2-VP-MBAm-AA) nanocomposite

##### Synthesis of $\text{TiO}_2$ nanoparticle

Initially  $\text{TiO}_2$  NPs were provided in accordance to the procedure reported, previously [82]. Accordingly, aqueous solution of ammonium sulfate ( $1.5 \text{ mol L}^{-1}$ ) and titanium (IV) chloride ( $0.75 \text{ mol L}^{-1}$ ) were mixed to react. This reaction proceeded at  $75^\circ\text{C}$  and completed in 90 min. Upon completion of this reaction,  $\text{NH}_4\text{OH}$  ( $2.5 \text{ mol L}^{-1}$ ) was gradually added under vigorous stirring until the pH of mixture was reached to 7. Then, the obtained solid was filtered off, washed with water/ethanol and dried at  $60^\circ\text{C}$ . Then calcination of NPs was achieved at  $350^\circ\text{C}$  for 4 h which allowed to cool down to room temperature [83].

##### Preparation of $\text{TiO}_2$ -MAPTMS

For preparation of  $\text{TiO}_2$ -MAPTMS NPs, we followed our previously reported method [83]. Accordingly,  $\text{TiO}_2$  NPs (1g) were dispersed in dry toluene (30 ml) using ultrasonic bath for 15 min. Then, MAPTMS (2 ml) was added as a coupling agent, drop wise to the mixture and the solution was kept under  $\text{N}_2$  atmosphere at ambient temperature for 48 h with vigorous stirring. The final product was separated by centrifugation and washed with toluene twice. Then modified  $\text{TiO}_2$  NPs were dried under vacuum at  $60^\circ\text{C}$  for 24 h.

##### Preparation of $\text{TiO}_2$ /poly (2-VP-MBAm-AA)

To provide hydrogel in 1:0.2:1 mole ratios, 2-VP, MBAm and *t*-BuA,  $\text{TiO}_2$ -MAPTMS (0.5 g) were

dissolved in DMSO (15 ml) and dispersed using ultrasonic bath for 15 min, under stirring and  $\text{N}_2$  purging for the same time, 2-Vp, (3 ml), *t*-BuA (4.1 ml) and MBAm (0.9 g) were added to the reaction mixture and stirred for 2 h. Ultimately, the resulting solution was heated up to  $80^\circ\text{C}$  with subsequent addition of AIBN (0.08 g). The polymerization was occurred in 2 h. The obtained hydrogel was washed several times with EtOH for the removal of unreacted monomers and then dried at  $50^\circ\text{C}$ . To hydrolyze the obtained hydrogel, the dried hydrogel (1g) was poured into the reaction vessel contained  $\text{CH}_2\text{Cl}_2$  (40 ml) and TFA (5 ml). Upon stirring the mixture in 24 h, the hydrolyzed hydrogel was washed with EtOH/ $\text{H}_2\text{O}$  and dried at  $60^\circ\text{C}$  [83].

##### Preparation of Cu(I) immobilized onto $\text{TiO}_2$ /poly (2-VP-MBAm-AA)

CuI (0.247 g) was dissolved in dry  $\text{CH}_3\text{CN}$  (2 ml) under ultrasonic and stirred for a while to obtain a transparent light yellow solution. Then DMF (20 ml) was added at ambient temperature to obtain CuI NPs [102-105]. It was then transferred into a 100 ml round-bottom flask containing dry polymer-supported (1 g). Then the mixture was magnetically stirred at reflux temperature for 5 h under a nitrogen atmosphere. The  $\text{TiO}_2$ /poly (2-VP-MBAm-AA)-CuI as a heterogeneous catalyst was filtrated and washed with  $\text{CH}_3\text{CN}$  ( $2 \times 20 \text{ ml}$ ) and dried under vacuum at  $60^\circ\text{C}$  for 24 h.

##### General procedure Synthesis of 1,4-disubstituted 1,2,3-triazoles: General procedure

In a round-bottom flask, an appropriate  $\alpha$ -halogenoketone (1 mmol) or benzyl halide (1 mmol) (5a–e), a suitable alkyne (1 mmol) (6a–c), sodium azide (1.1 mmol), and water (10 ml) were placed. Then,  $\text{TiO}_2$ /poly (2-VP-MBAm-AA)-CuI catalyst 4 (0.02 g) was added (Fig. 1), and the

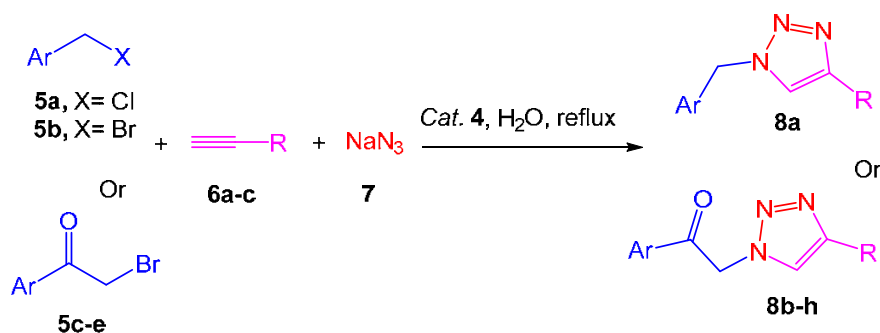


Fig. 1. Regioselective synthesis of 1,4-disubstituted-1H-1,2,3-triazoles using  $\text{TiO}_2$ /poly (2-VP-MBAm-AA)-CuI.

suspension was magnetically stirred under reflux for the appropriate time. The progress of the reaction was monitored by TLC (using *n*-hexane: ethyl acetate; 7:3 as eluent). Upon the completion of the reaction, the resin was filtered off and washed with hot EtOH. The recovered catalyst was washed with acetone, dried under reduced pressure at 70 °C for 3 h and stored for being employed in another reaction. Upon evaporation of the solvent of the filtrate, a solid was obtained which was recrystallized from hot EtOH to give the pure products in high yields. All the obtained triazoles (8a–h) were known and their physical data were compared with those of authentic samples and were found being identical [84–86, 106–110].

## RESULTS AND DISCUSSION

### Preparation and characterization of $\text{TiO}_2$ /poly (2-VP-MBAm-AA)

The  $\text{TiO}_2$  nanoparticles were initially provided in accordance with the procedure reported in the literature, previously [82] followed by

modification using MAPTMS. Then,  $\text{TiO}_2$ -MAPTMS react with 2-vinylpyridine, methylenbisacrylamide (MBAm) and tert-butyl acrylate (*t*-BuA) to form  $\text{TiO}_2$ /poly (2-VP-MBAm-AA) for being examined as a polymeric support (Fig. 2) The structure of product of each step was confirmed by FT-IR spectroscopy, X-ray diffraction, SEM images and thermogravimetry analysis [83].

### Preparation and characterization of the catalyst

Poly(vinyl pyridine) was known as a reactive species due to its high nucleophilicity but weakly basic due to ring nitrogen. Then, CuI NPs were supported to the synthesized above mentioned polymer support. In order to prevent agglomeration of the nanoparticles, Cu(I) NPs were synthesized *in situ* and then refluxed with polymer support under  $\text{N}_2$  atmosphere in DMF [111]. In this way, Cu(I) NPs were immobilized onto polymer support to obtain polymer-supported CuI nanoparticle catalyst (Fig. 2). As expected, the  $\text{TiO}_2$ /poly (2-VP-MBAm-AA)-CuI NPs were insoluble in all common organic

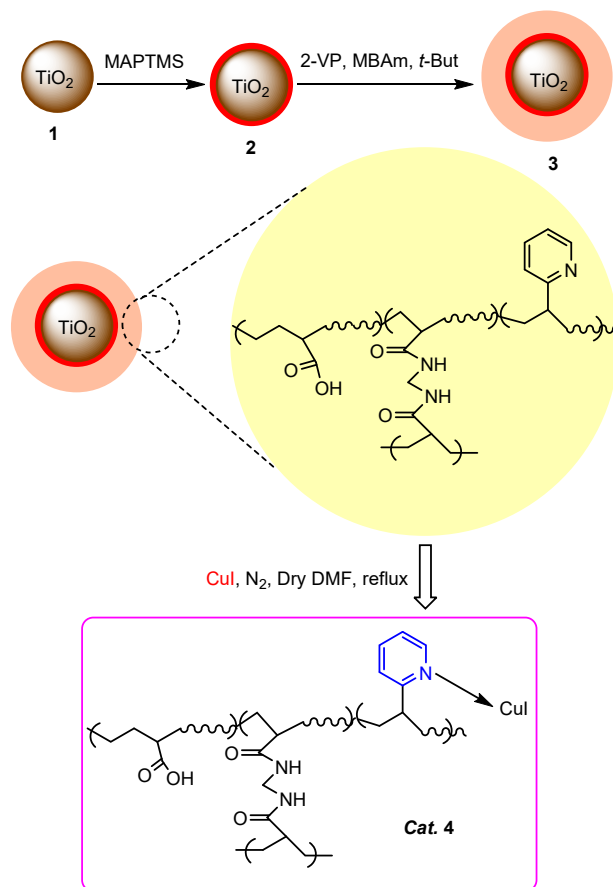


Fig. 2. Preparation of  $\text{TiO}_2$ /poly (2-VP-MBAm-AA)-CuI catalyst.

solvents thus, its structural characterization was limited to obtain their SEM, EDX, and ICP analysis.

The SEM of the TiO<sub>2</sub>/poly (2-VP-MBAm-AA)-CuI NPs (Fig. 3) vividly illustrated that the Cu(I) nanoparticles were homogeneously supported on the prepared polymer surface. The average size of Cu(I) NPs was estimated to be 43.85-75.24 nm.

Energy dispersive spectroscopy analysis (EDX) data for the TiO<sub>2</sub>/poly (2-VP-MBAm-AA)-CuI nanocatalyst is illustrated given in Fig. 4. The EDX data confirms that polymer matrix is containing Cu(I) NPs onto its surface. This data along with other aforementioned data such as SEM and FT-IR approved the attachment of Cu(I) NPs onto TiO<sub>2</sub>/

poly (2-VP-MBAm-AA).

The FT-IR spectrum of our sample was found identical to the already reported for TiO<sub>2</sub> nanoparticles, TiO<sub>2</sub>-MAPTMS, TiO<sub>2</sub>/poly (2-VPMBAm-*t*-BuA) nanocomposite [83] is shown in Fig. 5. As it can be seen clearly in Fig. 5a, the absorption broad bands below 800 cm<sup>-1</sup> and the broad peak in 3038 cm<sup>-1</sup> can be assigned to the Ti-O bond vibration and hydroxyl groups of TiO<sub>2</sub> nanoparticles, respectively [112]. On the other hand, the peaks in 956 cm<sup>-1</sup>, 1639 cm<sup>-1</sup>, 1712 cm<sup>-1</sup> and 2879-2919 cm<sup>-1</sup> can be assigned to the Ti-O-Si, C=C and C=O moieties, respectively (Fig. 5b) [113-115]. In conclusion, the preparation and

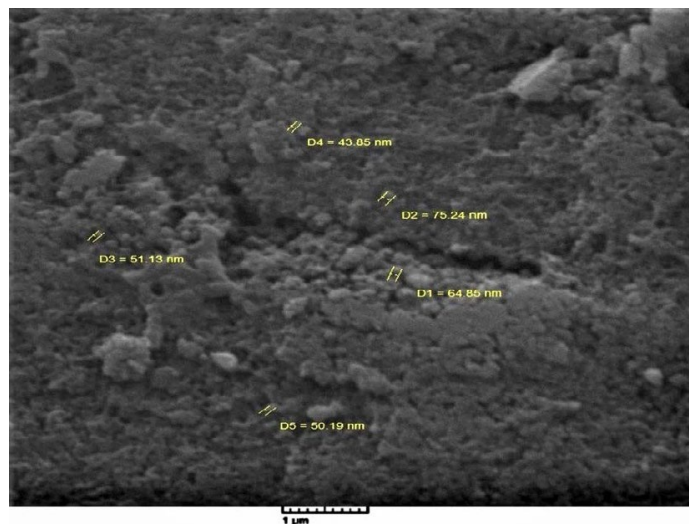


Fig. 3. SEM image of TiO<sub>2</sub>/poly (2-VP-MBAm-AA)-CuI.

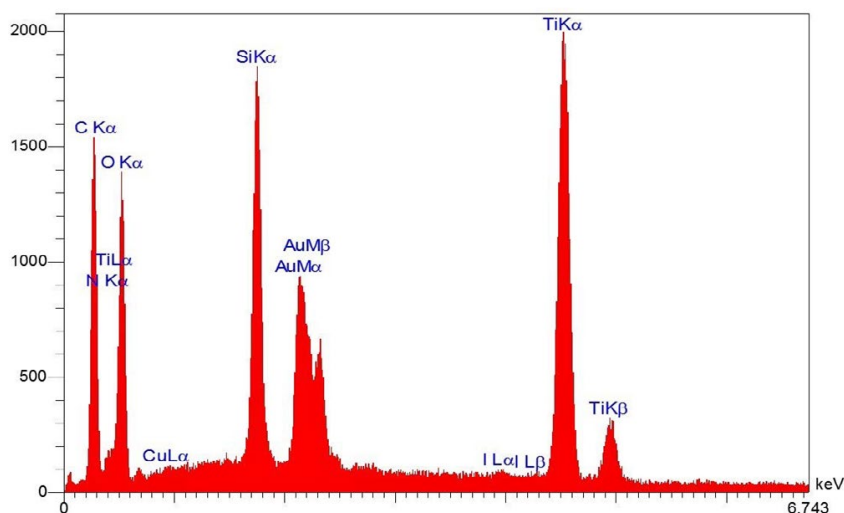


Fig. 4. EDX data of TiO<sub>2</sub>/poly (2-VP-MBAm-AA)-CuI.

modification  $\text{TiO}_2$ -MAPTMS has been approved.

The fruitful polymerization can be realized and approved by the appearing and presence of new peaks in IR spectrum shown in Fig. 5c. The other characteristic bands at  $1732\text{ cm}^{-1}$  attributed to ester groups of *t*-BuA, at  $1659\text{ cm}^{-1}$  associated to amide carbonyl groups and  $1533\text{ cm}^{-1}$  assigned to the N-H bond of MBAm bending vibration [116],  $1593\text{ cm}^{-1}$  and  $1557\text{ cm}^{-1}$  corresponding to the pyridine-stretching vibrations [117, 118]  $1149\text{ cm}^{-1}$ , and  $1248\text{ cm}^{-1}$  associated to CO-C and C-N bonds, respectively [118, 119]. Upon the hydrolysis of *t*-BuA, appearance of a new peak at  $1692\text{ cm}^{-1}$  clearly the presence of carboxyl moieties. Notably, the intensity of C-O-C at  $1149\text{ cm}^{-1}$  was

also reduced and can be clearly observed.

FT-IR spectrum (Fig. 6) of prepared Cu(I) NPs catalyst revealed the interaction of  $\text{TiO}_2$ /poly (2-VP-MBAm-*t*-BuA) with Cu(I) NPs by observation of changes and shifts for the positions of several bands.

*Determination of the copper content in  $\text{TiO}_2$ /poly (2-VP-MBAm-AA)-Cu(I)*

The Cu content of polymer was evaluated upon treatment of  $\text{TiO}_2$ /poly (2-VP-MBAm-AA)-Cu(I) (100 mg) with a mixture of Conc. HCl/HNO<sub>3</sub> (1:1, 10 ml) by digestion of the copper species. The mixture was transferred into a volumetric flask (100 ml), diluted and then was analyzed by ICP. The Cu concentration

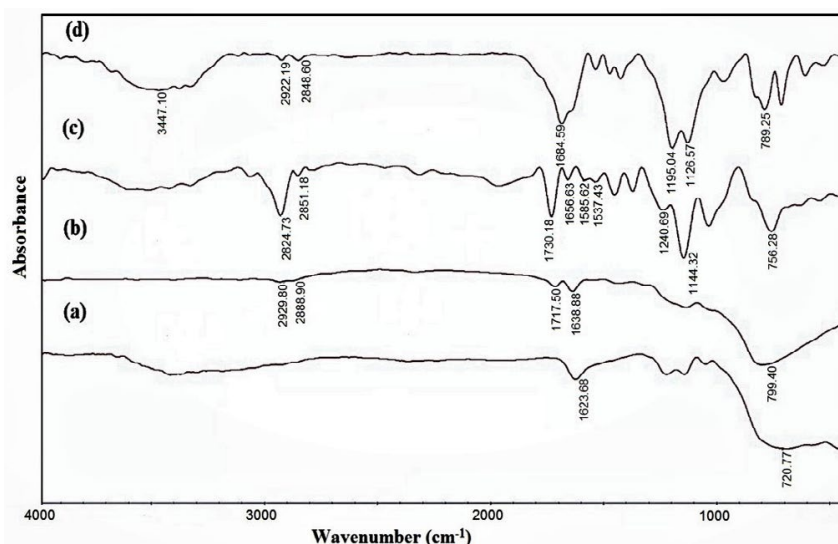


Fig. 5. FT-IR spectra of (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2$ -MAPTMS, (c)  $\text{TiO}_2$ /poly (2-VP-MBAm-*t*-BuA) and (d)  $\text{TiO}_2$ /poly (2-VP-MBAm-AA).

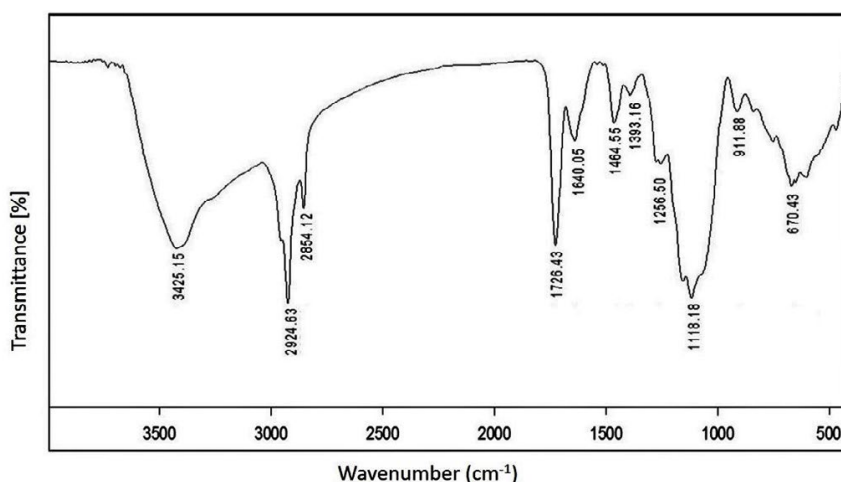


Fig. 6. FT-IR spectrum of prepared  $\text{TiO}_2$ /poly (2-VP-MBAm-AA)-CuI.

was determined from the atomic emission (324.754 nm) by reference to a linear ( $R = 0.99$ ) calibration curve of (1–4 ppm) of CuI provided by a procedure similar to the sample preparation. The Cu content was defined being 6.6 % w/w. The same procedure was employed to disclose the extent of leaching from the immobilized catalyst after five consecutive runs.

#### Catalytic activity of the catalyst in the click reaction

Initially, a mixture of benzylchloride (1 mmol), sodium azide (1.1 mmol), and phenylacetylene (1 mmol) was chosen as a model reaction in the presence of catalytic amount of  $\text{TiO}_2/\text{poly}(2\text{-VP-MBAm-AA})\text{-CuI}$  and in different solvents (Table 1).

Although the 'click' azide-alkyne cycloaddition reaction has been successfully examined in a wide range of common organic solvents, but as illustrated in Table 1, it can be seen that water acts as the most efficient solvent in comparison to the others thus we used water as the solvent of choice. We focused our attention on the reaction in pure water, since this is the solvent of choice in green chemistry as well as being accessible

virtually free of cost. Thus, to test the substrate scope of reaction in water various terminal alkynes and  $\alpha$ -halo ketones or benzyl halides were successfully examined, establishing the generality of our methodology (Table 2).

#### Recyclability of the catalyst

It is worthwhile to mention that for the resin, extensive mechanical degradation after its catalytic activity was not observed as for a real heterogeneous catalysis. The supported catalyst should not leach into the reaction mixture since the reusability of the catalyst is much in concern. To study these properties for our new catalytic system, we selected the reaction of benzyl chloride, phenyl acetylene, and sodium azide as a model reaction. We observed no appreciable loss in the catalytic activity after five consecutive runs (Fig. 7), and no need for reloading the catalyst. As a matter of fact, the difference in the Cu content for the fresh and recycled catalyst was not significant after the five run, confirming a low leaching for our new catalyst system.

Table 1. The effect of solvent on model reaction at refluxing conditions <sup>a</sup>.

Entry	Solvent	T(min)	Yield (%) <sup>b</sup>
1	$\text{CH}_3\text{CN}$	105	82
2	$\text{CH}_2\text{Cl}_2$	95	74
3	EtOH	80	84
4	EtOH/ $\text{H}_2\text{O}$ (1:1)	65	91
5	$\text{H}_2\text{O}$	60	90

a) Reaction condition:  $\alpha$ -Halogenoketone or benzyl halide (1mmol), sodium azide (1.1 mmol), phenylacetylene (1 mmol) and 0.02 g of catalyst  
b) Isolated yields

Table 2. Optimal reaction conditions for the synthesis of 1,4- disubstituted-1*H*-1,2,3-triazoles 8a-h<sup>a</sup>.

Entry	Ar (5a-e)	R (6a-6c)	Product (8a-h)	Time (min)	Yield (%) <sup>b</sup>	MP (°C) (Lit. [ref])
1	Ph (5a) X = Cl	Ph (6a)	8a	60	90	126-129 (128-130 [72])
2	Ph (5b) X = Br	Ph (6a)	8a	67	92	126-129 (128-130 [72])
3	Ph (5c)	Ph (6a)	8b	80	91	170-171 (169-170 [74, 51])
4	4-Me- $\text{C}_6\text{H}_4$ (5d)	Ph (6a)	8c	90	88	157-160 (158-160 [75])
5	4-Me- $\text{C}_6\text{H}_4$ (5d)	$\text{C}(\text{CH}_3)_2\text{OH}$ (6b)	8d	115	84	152-154 (153-155 [76])
6	Ph (5c)	$\text{CH}_2\text{OH}$ (6c)	8e	120	81	113-116 (115-118 [75])
7	4-Me- $\text{C}_6\text{H}_4$ (5d)	$\text{CH}_2\text{OH}$ (6c)	8f	125	80	179-181 (179-182 [76])
8	4-Br- $\text{C}_6\text{H}_4$ (5e)	$\text{C}(\text{CH}_3)_2\text{OH}$ (6b)	8g	110	76	170-173 (169-171 [76])
9	4-Br- $\text{C}_6\text{H}_4$ (5e)	$\text{CH}_2\text{OH}$ (6c)	8h	100	88	155-157 (157-160 [50])

a) Reaction condition:  $\alpha$ -Halogenoketone or benzyl halide (1mmol), alkyne (1mmol), sodium azide (1.1 mmol), water (10 ml), and catalyst 4 (0.02 g) under reflux  
b) Isolated yields



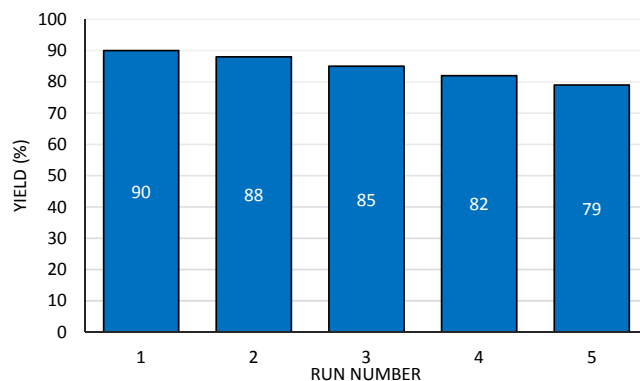


Fig. 7. The recyclability of the  $\text{TiO}_2/\text{poly (2-VP-MBAm-AA)-CuI}$  in the preparation of 8a.

## CONCLUSIONS

In this summary, for the first time, we developed a Cu(I), catalytic system with the heterogeneous catalysts merits, for example rapid and easy separation of the catalytic system by simple filtration as well as efficient recovery and reusing it in a one-pot synthesis of 1,4-disubstituted-1H-1,2,3-triazoles *via* click reaction of terminal alkynes,  $\alpha$ -halo ketones and  $\text{NaN}_3$  in the presence of a new recyclable catalyst at reflux temperature in water as the greenest and most abundant solvent. The 1,2,3-triazoles were obtained regioselectively in satisfactory yields purities, confirmed by comparison of their physical with those of authentic samples and were found being identical.

Furthermore, using water as solvent, operational simplicity, ease of work-up and clean procedure, make this newly introduced catalyst as an useful and important additional strategy to the already reported protocols for the regioselective synthesis of 1,2,3-triazoles. Our observation showed that this catalyst give satisfactory yields in reasonable reaction times and can be used for five consecutive runs, with very low leaching of the immobilized Cu(I). Therefore, this modified  $\text{TiO}_2/\text{poly (2-VP-MBAm-AA)-CuI}$  can be considered as an attractive support in the synthesis of polymer supported catalysts in other organic transformations especially those catalyzed by Cu(I). The produced Cu(I) NPs catalyst was characterized by FT-IR, SEM, EDX, ICP-OES methods.

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## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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