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#### Abstract

Nowadays, carbon dioxide fixation has received much more attention for its imminent application as an abundant C1 source and a range of important fine chemicals which can be manufactured *via* this fixation. Here, Cu NP decorated porous organic polymer-based (Cu-NPs@TzTa-POP) material was prepared by a simple in-situ process. The catalyst was characterized by UV-Vis spectra, FTIR spectra, HR-TEM, PXRD, N<sub>2</sub> adsorption-desorption, TG-DTA, XPS, AAS analysis, etc. The synthesized heterogeneous catalyst showed excellent activity in atmospheric carbon dioxide fixation reaction to produce N-methylated products from aromatic/ heterocyclic amines in the existence of polymethyl-hydrosiloxane (PMHS) as reducing agent at 80°C within 12 h of reaction. Through this catalytic N-methylation reaction, we got up to 98% yield of the product with turnover frequency from 18 to 42 h<sup>-1</sup>. Besides, the catalyst is also very stable for the formation of primary carbamates from alcohols using eco-friendly carbonylating agent urea. A diverse type of alcohols (such as benzylic alcohols, phenols, heterocyclic alcohols as well as aliphatic alcohols) showed very much acceptance to this catalytic reaction and produced moderate to the excellent yield of respective carbamate products under ambient reaction conditions. Moreover, Cu-NPs@TzTa-POP is effortlessly recyclable and reusable without extensive loss of active copper metal centre for many catalytic rounds (up to six catalytic rounds were examined).

### Introduction

Carbon dioxide, is the main green house gas, is also considered as cheap, abundant, renewable, sustainable and non-toxic carbon fed stock for the production of fuels and valuable organic compounds<sup>1</sup>. The catalytic carbon dioxide reduction into energy-enrich small compounds like CO, HCOOH, CH<sub>4</sub>, and CH<sub>3</sub>OH has been in rapid improvement in last decade<sup>2</sup>. Not only that, fixation of carbon dioxide via reduction onto amines in order to make a new C-N bond for the formation of methylamines or formamides has also gaining a growing attention today.<sup>3</sup> Methylamines are broadly used as solvents and in synthesis of agrochemicals, medicines, dyes, perfumes, and so on.<sup>4</sup> Since 1970, hydrogen has been utilized for reductive CO<sub>2</sub> fixation in amines to produce methylamines or formamides.<sup>5</sup> But drastic reaction conditions like high pressure of hydrogen and carbon dioxide, high temperature of reaction and costly metal-based catalysts are generally required in these methodologies. Recently scientists have found that, catalytic CO<sub>2</sub> reduction could be performed easily under mild conditions by using boranes<sup>6</sup> or hydrosilanes<sup>7</sup> as hydrogen source. Till date various catalytic systems have been already reported where hydrosilanes is used for CO<sub>2</sub> reduction in selective N-methylation reaction.<sup>8</sup> In most of the cases, phenylsilane was used as reductive agent but it is more costly than PMHS (polymethylhydrosiloxane), which is copious chemical waste having no toxicity, cheap, and impressive resistant to moisture.9 Hence use of PMHS as reducing agent for

 $CO_2$  fixation in amines will be very attractive. Xia and co-workers published a paper where *N*-Methylation of amines with carbon dioxide using PMHS as reductant in presence of DBU (base) catalyst.<sup>10</sup> Here the catalytic process was performed under homogeneous conditions. As a result, recyclability and reusability of the catalyst remains challenging. Henceforth we have designed and synthesized a trizinetriamine derived porous organic polymer frame work incorporated copper nanoparticles (Cu-NPs@TzTa-POP) which produced N-methylated product via catalytic reductive fixation of  $CO_2$  in amines using PMHS as a reducing agent under ambient and heterogeneous reaction conditions.

Carbamates are very essential class of organic compounds that usually found in drugs and medicines (such as albendazole, retigabine, flupirtine, and physostigmine etc.),<sup>11</sup> agricultural products (as antiviral agents, bactericides, pesticides and herbicides),<sup>12</sup> cosmetics, organic fine chemicals, biologically active compounds and polymer compounds.<sup>13</sup> Again carabamtes are used in organic synthesis for the protection of amino groups of amino acids in peptides synthesis chemistry.<sup>14</sup> Traditionally carbamates are synthesized from amines and alcohols using phosgene (COCl<sub>2</sub>) as carbonyl source.<sup>15</sup> But this protocol suffer from the limitations of long reaction duration, low atom economy, large amount of toxic waste production, utilization of harmful reagent (phosgene) and insufficiency for N-unsubstituted (primary) carbamates etc.<sup>15,16</sup> During current few years, immense attentions have been paid to discover eco-friendly pathways that use other carbonyl sources such as isocyanides,<sup>17</sup> cyanate or isocyanate salts,<sup>18</sup> azides,<sup>19</sup> Nacylbenzotriazoles,<sup>20</sup> carbonate esters,<sup>21</sup> 1,1,1-trichloromethyl

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formate (diphosgene),<sup>22</sup> trichloroacetylchloride,23 1,1carbonyldiimidazole (CDI),<sup>24</sup> dialkylazodicarboxylate,<sup>25</sup> CO<sub>2</sub><sup>26</sup>, and amides<sup>27</sup> in place of phosgene for carbamate synthesis. Although alternate carbonyl source is used in these protocols, these processes have the disadvantages of multi-step procedures, drastic reaction conditions, utilization of toxic metal-based catalysts, strong bases and expensive ligands. Now our interest is to develop an ecofriendly, proficient and cost effective protocol for production of carbamate compounds. The use of polyurea/urea as carbonyl sources for the production of carbamates is considered as safe and green.<sup>28</sup> Beller and co-workers published carbamoylation reaction for primary carbamates production from urea and alcohols by eco-friendly Lewis-acidic FeBr<sub>2</sub> catalyst utilizing under homogeneous conditions.<sup>29</sup> But use of homogeneous FeBr<sub>2</sub> catalyst leads to reusability and recyclability problems. Inaloo et. al. reported couple of publications where polyurea/urea was employed as carbonyl sources for this derivatives preparation.<sup>30</sup> Although heterogeneous catalysts are used in those reports, the reacting conditions are not mild in all those cases. Recently our group synthesized a polymer supported heterogeneous catalyst. [Fe<sup>II</sup>(Anthra-Merf)] that can synthesize primary carbamates via carbamoylation reaction of urea with alcohols at 120°C in 6.5 h<sup>31</sup>. Here Cu-NPs@TzTa-POP catalyst is used in synthesis of primary carbamates from urea and alcohols at 80°C within 4 h of reaction.

Therefore a trizinetriamine derived porous organic polymer embedded copper nanoparticles (Cu-NPs@TzTa-POP) catalyst is synthesized for the production of N-methylated products as well as primary carbamates under mild reaction conditions with high yield of isolated products.

### Experimental

## Synthesis of Copper Nanoparticles decorated TriazineTriamine derived Porous Organic Polymer catalyst (Cu-NPs@TzTa-POP)

500 mg of Triazine Triamine based Porous Organic Polymer (TzTa-POP) was sonicated in 100 ml distilled water till the polymer dispense uniformly. After that, 3 ml aqueous solution of copper acetate was added drop by drop to the solution under moderate stirring and the temperature was raised to  $80^{\circ}$ C. After 1h of stirring,  $500 \ \mu$ L of hydrazine was added to the reaction mixture and stirring was continued for another 2h. The solid product obtained was washed with water and ethanol and dried under vacuum. The details procedure of synthesis of the catalyst is depicted here in **Scheme 1** as pictorial representation.



Scheme 1. Pictorial presentation of synthesis of Cu-NPs@TzTa-POP catalyst.

General procedure of catalytic synthesis of N-methylated products

In a 50 ml round bottom flask, 5 mmol of respective amine was dissolved in 5 ml acetonitrile solvent. In this mixture 2 equivalent of

polymethylhydrosiloxane (PMHS) was added. Under stirring condition 20 mg of Cu-NPs@TzTa-POP catalyst wasonixed into this reaction solution and the temperature was raised to 80°C. The system was fitted with a CO<sub>2</sub> balloon. Thin layer chromatography method was used to observe advancement of the reaction. After completion of reaction, the mixture was diluted with ethyl acetate and washed with brine solution several times. Lastly dry sodium sulfate was used to absorb the excess water present in the filtered mixture. Finally the desired product was obtained via performing purification by thin layer chromatography (pet ether: ethyl acetate 10:1) method.

## General procedure of catalytic synthesis of primary carbamates from urea

In a 25 ml RB, 4 mmol of urea was treated with 5 mmol of alcohol derivatives in 1,4-dioxane (4 ml) solvent. 20 mg of catalyst Cu-NPs@TzTa-POP were added to the mixture. After 4 hours of continuous stirring at 80°C, the reaction mixture was filtered to separate the catalyst. With the filtrate, work up was performed by ethyl acetate and brine solution for several times. At last, the remaining water part was absorbed by sodium sulphate and purified organic layer was preserved and analyzed by <sup>1</sup>H NMR and IR spectra.

## **Results and discussion**

#### Characterization of Cu-NPs@TzTa-POP material

#### FT-IR spectra

The FTIR spectrum of ligand TzTa-POP and Cu-NPs@TzTa-POP catalyst are described in **Figure 1.** The corresponding stretching frequencies provide a proof behind the structure of the obtained porous organic polymer skeletons. In FTIR spectra of TzTa-POP, the bands observed at 1622 and 1507 cm<sup>-1</sup> were arises due to the triazine rings in the synthesized polymer frame.<sup>32</sup> The stretching frequencies at 1255 and 1074 cm<sup>-1</sup> were found because of the occurrence of aromatic ether of the benzoxazine ring in polymer moiety for C-O-C asymmetric and symmetric stretching vibrations, respectively.<sup>33</sup> Again the characteristics vibrations of phenyl ring connected to oxazine ring appeared at 945 cm<sup>-1</sup>.<sup>33</sup> All these respective bands were also seen in the spectra of Cu-NPs@TzTa-POP catalyst but in slightly shift their position validates the attachment of copper nanoparticles over the TzTa-POP.



Fig. 1 FT-IR spectra of TzTa-POP and Cu-NPs@TzTa-POP catalyst.

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#### PXRD of Cu-NPs@TzTa-POP catalyst

The crystalline nature of the synthesized Cu-NPs@TzTa-POP catalyst was defined through powder X-ray diffraction analysis experiment. This represented some strong peaks in the range of 5 to 90° 20 value (**Figure 2**). In this figure the Bragg reflection peaks appeared at 43.0083°, 50.1654°, 73.9181° 20 value, with the corresponding planes (111), (200) and (220) of Cu(0) nanoparticles respectively. From this lattice planes it is confirmed that copper formed a face centered cubic lattice (fcc).<sup>34</sup> The existence of a broad peak near 35° 20 value suggest existence of TzTa-POP framework in the catalyst. TzTa-POP material showed a broad peak centred at 32° 20 value indicates amorphous nature of the material (**Figure S1**).



Fig. 2 Powder X-ray diffraction pattern of Cu-NPs@TzTa-POP catalyst.

## High Resolution Transmission Electron Microscopic (HR TEM) analysis

The HR TEM micrographs of Cu-NPs@TzTa-POP catalyst in Figure 3(a-d) represent with various magnifications. The images substantiate that the material holds multilayered structure with homogeneously spread pores on its surface. From these images it is confirmed that in catalyst copper nanoparticles deposited on its surface. The calculated d-spacing (Figure 3d) marked by red circle is 0.2332 nm which corresponds to (111) planes of Cu(0) NPs.<sup>35</sup> Different size of copper nano particles (ranging from 2-20 nm) are distributed on surface of TzPa-POP (figure 3e). The particle size distribution plot is given in figure 3f.

# Energy dispersive X-ray analyses (EDAX) of Cu-NPs@TzTa-POP catalyst

For further clarification of presence of copper metal on synthesized porous organic polymer surface we have carried out EDAX analysis of the catalyst. **Figure 4** firmly demonstrates the existence of elements carbon, oxygen and nitrogen along with copper metal.

#### XPS analysis

The determination of oxidation state of Cu and the attachment of Cu metal with the other elements in the synthesized Cu-NPs@TzTa-POP catalyst was properly searching out through XPS analysis. A full range XPS analysis is given in **Figure 5** whereas; the narrow range analysis is represented in **Figure 6a-d** for copper, carbon, nitrogen, oxygen respectively. In the spectrum the strong binding energy peak are observed at 952.2 and 932.4 eV, assigned the two different Cu(0) level energy, Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$  respectively. The difference of the two binding energy peaks was represented in Table 1.<sup>34</sup> These core levels could be resolved into two, Cu (0)/Cu (I) as a major and Cu(II) as minor species. In the Cu 2p spectrum, no

satellite peaks were detected to somehow validate the particulars components comprising the line of Cu  $2p_{3/2}$  to the states Cu<sup>0</sup> and Cu<sup>+</sup> (Fig. S2, ESI<sup>+</sup>). Having regard to the XPS results demonstrating the coexistence of Cu<sup>0/1+</sup> as a major species and Cu<sup>2+</sup> as a minor species on the surface of the as-obtained POP, one is willing to concede that such combined species of various oxidation states appear on the surface of the material. The formation of Cu NPs was assessed by XRD technique, which supports the synthesis of Cu NPs owing to the absence of Cu(1) diffraction peaks (i.e. Cu<sub>2</sub>O). We can conclude that the analysis of XRD and XPS precisely indicates the chemical integrity of Cu NPs decorated POP.<sup>36</sup> The experimental result gave carbon, nitrogen, oxygen 1s core level binding energy peak at 284.2, 398.3, 532.3 eV respectively.







Fig. 4 EDAX spectrum of Cu-NPs@TzTa-POP catalyst.

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homogeneously dispersed the materials in acetonitrile solvent individually. A sharp peak appear at ~207 and 102069 mon for 2 both ligand and catalyst moiety due to presence of  $\pi$ - $\pi$ \* transition.<sup>32</sup> Many other absorption peaks indicate other transitions hold by the highly conjugative systems.



Fig. 7 adsorption desorption curve of Cu-NPs@TzTa-POP at 77 K. Pore size distribution plot (inset).



Fig. 8 UV-Vis spectroscopy of TzTa-POP and Cu-NPs@TzTa-POP catalyst.

#### TGA analysis of TzTa-POP ligand and Cu-NPs@TzTa-POP catalyst

To investigate thermal stability of porous organic polymer and TzTa-POP incorporated copper nano particle (Cu-NPs@TzTa-POP), thermogravimetric analysis was done under N<sub>2</sub> atmosphere with the heating rate of 10 °C/minute (**Figure 9**). For TzTa-POP support the weight loss occur from 100 °C to 256 °C but for Cu-NPs@TzTa-POP catalyst the weight loss occur in the range of 115 °C to 455 °C. It concludes from the thermogram that beyond 455 °C the decomposition of catalyst is completely done and the stability of catalyst increase with the incorporation of Cu nanoparticle onto TzTa-POP surface.

#### Atomic absorption spectroscopy analysis

Atomic absorption spectroscopy analysis was monitored to measure the amount of copper metal present on TzTa-POP surface.

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Fig. 5 Full range X-ray photoelectron spectroscopy of Cu-NPs@TzTa-POP catalyst.



Fig. 6 Narrow-range XPS spectra of Cu-NPs@TzTa-POP containing elements (a) Cu 2p, (b) C 1s, (c) N 1s, and (d) O 1s.

Table 1. XPS data of catalyst Cu-NPs@TzTa-POP

Sample name	Cu2p <sub>1/2</sub> peak (eV)	Cu2p <sub>3/2</sub> peak (eV)	Peak difference (eV) Cu (2p <sub>1/2</sub> -2p <sub>3/2</sub> )
Cu-NPs@TzTa-POP	952.2	932.4	19.8

#### N<sub>2</sub> Adsorption-Desorption study

In order to measure the pore size, surface area and pore volume of the synthesized catalyst we have carried out BET analysis of the Cu-NPs@TzTa-POP. The obtained isotherm is typical type IV isotherm having a hysteresis loop in the pressure range of  $0.8 < p/p^0 < 1.0$  clearly indicates that the material is mesoporous in nature (**Figure 7**).<sup>33,37</sup> Through BJH method, pore size distribution curve was calculated and the result showed that the catalyst have the average pore size of 19 nm (inset of **figure 7**). The multi point BET surface area and total pore volume of Cu-NPs@TzTa-POP are 228.501 m<sup>2</sup>/g, 0.927 cc/g respectively.

#### UV-Vis spectroscopy of Cu-NPs@TzTa-POP catalyst

The UV-Vis spectra of both TzTa-POP ligand and Cu-NPs@TzTa-POP catalyst is represented in **Figure 8**. The data was recorded by

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58 59 60 It was observed that nearly 4.86% of the metal is loaded on the catalyst surface.



Fig. 9 TGA plot of TzTa-POP and Cu-NPs@TzTa-POP catalyst.

### Catalysis

## Reaction conditions optimization for benzimidazolone synthesis

Catalytic N-methylation reaction via carbon dioxide fixation in presence of Cu-NPs@TzTa-POP catalyst



**Scheme 2.** Catalytic N-methylation reaction of amines through carbon dioxide fixation.

Catalytic N-methylation reaction of amines was carried out in presence of our synthesized Cu-NPs@TzTa-POP catalyst under 1 atmospheric CO<sub>2</sub> pressure in attendance of one reducing agent (Scheme 2). N-methylaniline was chosen as model substrate to optimize the catalytic reaction's conditions. Primarily we commence the reaction by using 5 mmol of N-methylaniline, 2 equivalent of polymethylhydrosiloxane (PMHS) as reducing agent under CO<sub>2</sub> (1 atm) at 80°C in dioxane (5 ml) solvent with the help of 15 mg Cu-NPs@TzTa-POP catalyst. It was very inspiring that the reaction was worked and we got 76% GC yield of N,N-dimethylaniline after 12h of reaction. Then solvent effect on the reaction was scrutinized by using various type of solvents (Table 2, Entries 1-8). From table 2 it is very clear that almost all solvents gave more or less amount of corresponding product but acetonitrile (MeCN) showed the maximum efficiency as solvent in this reaction (Table 2, Entry 5). Using MeCN as solvent the reaction was proceed at RT (room temperature), after 12h of reaction we got only 25% yield of the product (Table 2, Entry 9). Again the same reaction was performed at 50°C, although better yield of product (69%) (Table 2, Entry 10) was obtained as compare to the previous reaction but maximum product yield was achieved from 80°C temperature reaction (Table 2, Entry 5).

**Table 2.** Effect of solvents and temperature in the catalytic N-methylation reaction of N-methylaniline

	Entry	Solvent	Temperature (°C)	Time (h)	GC yield (%)
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1	1,4-dioxane	80	12	View Article Onlin
2	Tolune	80	DC <b>1</b> 210.10	039/D0NJ02798
3	DMF	80	12	42
4	DMSO	80	12	46
5	MeCN	80	12	91
6	DCM	80	12	58
7	THF	80	12	-
8	NO solvent	80	12	-
9	MeCN	r.t.	12	25
10	MeCN	50	12	69

Reaction occurred at atmospheric  $CO_2$  pressure, N-methylaniline (5 mmol), PMHS (2 equivalent), Cu-NPs@TzTa-POP Catalyst (15 mg).

The reaction was harmonized by changing the amount of reducing agent and catalyst loading (Table 3). With enhancing catalyst amount from 10 to 20 mg, GC yield of the product was also rising from 49% to >99% (Table 3, Entries 1-3). In absence of catalyst, the reaction did not take place (Table 3, Entry 4). The amount of PMHS was used from 0.5 equivalents to 2.0 equivalents for the reaction (Table 3, Entries 5-8). Using 0.5 equivalents of PMHS, very little amount of product was appeared (Table 3, Entry 5). With increasing the amount of reducing agent, the yield of product was also increases and attain optimum value by utilization of 2 equivalents PMHS (Table 3, Entry 8). No product was obtained when the reaction was monitored without reducing agent (Table 3, Entry 9). When TzTa-POP without copper incorporation was used as catalyst 42% yield of desired product was observed (Table 3, Entry 10) and trace amount of product was obtained when copper acetate salt was used as catalyst (Table 3, Entry 11). Recently we have prepared a covalent organic framework supported copper (0) nanoparticles (Cu-NPs@COF) through similar methodology and used as efficient catalyst for CO<sub>2</sub> fixation reaction to produce 2-oxazoliinones and benzimidazoles.<sup>38</sup> In this catalysis the same Cu-NPs@COF material was used as catalyst in order to order to compare the efficiency of our present catalyst and the TriazineTriamine derived Porous Organic Polymer support. Cu-NPs@COF catalyst produced 81% yield of product (Table 3, Entry 12). Again the support of the catalyst Cu-NPs@COF i.e. COF yielded 38% of the product (Table 3, Entry 13). Since both support of the catalysts; TzTa-POP and COF gave considerable amount of desired product (42% and 38% respectively) whereas Copper(II)acetate produced only trace amount of product. So there is definitely a contribution of the support TzTa-POP on the catalytic reaction.

Table 3. Effect of catalyst loading and PMHS amount on the N-methylation reaction

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Entry	Catalyst	Amount of	GC yield of product
	amount (mg)	PHMS (equiv.)	(%)
1	10	2.0	49
2	15	2.0	72
3	20	2.0	>99
4	-	2.0	-
5	20	0.5	Trace
6	20	1.0	34
7	20	1.5	53
8	20	2.0	>99
9	20	-	-
10	20ª	2.0	42
11	20 <sup>b</sup>	2.0	Trace
12	20 <sup>c</sup>	2.0	81
13	2.0 <sup>d</sup>	2.0	38

**Reaction conditions:** N-methyl aniline (5 mmol), PMHS, CO<sub>2</sub> (1 atm), Cu-NPs@TzTa-POP catalyst, 80°C, 12h, aTzTa-POP as catalyst, <sup>b</sup>Copper acetate salt as catalyst, <sup>c</sup>Cu-NPs@COF as catalyst, <sup>d</sup>COF as catalyst.

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The rate of the reaction with respect to time in presence as well as in absence of Cu-NPs@TzTa-POP catalyst (Figure 10) was also studied in this circumstance. From the figure it is clearly noticeable that the reaction was performed in faster rate and completed within 12h in presence of catalyst. Whereas non-existence of catalyst in reaction mixture, the reaction was not progressed smoothly. After 15h of reaction, only 5% (approximately) yield of product was appeared.



Fig. 10 Study of rate of N-methylation reaction in presence and absence of catalyst.

Catalytic N-methylation reaction was carried out in presence of 20 mg Cu-NPs@TzTa-POP catalyst under atmospheric CO<sub>2</sub> pressure at 80°C in MeCN solvent with various aromatic and heterocyclic amines. All aromatic amines as well as heterocyclic amines smoothly go through this reaction and furnishes very good yield of desired product (Table 4). The given data of each entry are the mean value of three successive reactions. The collected results of all reactions are given in Table S1. Very high yield of desired product was obtained from N-methylaniline and N,4-dimethylaniline through this catalytic reaction (Table 4, Entries 1-2). Electron withdrawing group containing N-methylaniline (like 4-fluoro-Nmethylaniline) also produced very high yield (91.3%) of product in this reaction (Table 4, Entry 3). Again N-ethylaniline gave 93.7% yield of respective N-methyl product (Table 4, Entry 4) whereas diphenylamine produced relatively lower yield (61.3%) of the product due to presence of sterically crowding phenyl group (Table 4, Entry 5). The heterocyclic amines (such as morpholine, pyrrolidin-2-one) also very efficiently performed this catalysis reaction and gave us >92% yield of corresponding N-methyl product (Table 4, Entries 6,7).

Table 4. Substra	ates scope of o	catalytic N-me	ethylation	reaction
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E	Amines	Products	Time	Conv.	Yield	TOF	
n			(h)	(%) <sup>b</sup>	(%) <sup>c</sup> [%	(h <sup>-1</sup> )	
t					of		
r					isolated		
y					yield]		
1			12	100	>99	27.78	
		∧ N N			[96.3]		
					[]		
	1a	22					
2		20	10	100	>00	22.22	
2	ŃH	N.	10	100	299	55.55	
					[95.3]		
	$\sim$						
	1b						
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				DC	1: <b>19:133</b> 9/	D0NJ027980
	- 1c	2c				
4			9.5	100	98	35.09
	NH	N N			[93.7]	
	1d	2d				
5			12	65	97	18.05
	∧ NH				[61.3]	
	1e	2e				
6	0 NH	0 N-	8	100	98	41.67
	1f	2f			[94.3]	
7	HZ	N	8	100	97	41.67
	L∕=0	=0			[92.0]	
	1g	2g				

<sup>a</sup>Reaction conditions: substrate (5 mmol), PMHS (2 equiv.), Cu-NPs@TzTa-POP catalyst (20 mg, 0.015 mmol based on copper metal),  $CO_2$  (1 atm), MeCN (5 ml), 80°C; <sup>b</sup>GC conversion; <sup>c</sup>GC yield; TOF (turn over frequency)=no. of moles of the substrate being converted per mole of active site of the catalyst/time (in h).

Scheme 3 represents the probable mechanistic pathway for the formation of N-methylated products via carbon dioxide fixation of amines. The depicted mechanism is basically supported from the previously published literature.<sup>3c,39</sup> Initially copper metal of the catalyst activated Si-H bond of PMHS. Then carbon dioxide is incorporated into the bond. Since polymethylhydrosiloxane contains multiple Si-H bonds, it successfully provides hydrogen to the reaction medium for the reduction of carbonyl group to produce desired product.



Scheme 3. Probable route of catalytic synthesis of N-methylated products.

Catalytic synthesis of primary carbamates from alcohol and urea in presence of Cu-NPs@TzTa-POP catalyst



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Primary carbamates were synthesized by using various alcohols and urea in presence of the Cu-NPs@TzTa-POP catalyst (Scheme 4). The standardization of the catalysis reaction was monitored by taking benzyl alcohol as model substrate. First of all we performed a catalytic reaction by using benzyl alcohol (5 mmol), urea (4 mmol), Cu-NPs@TzTa-POP catalyst (15 mg) at 80°C in MeCN (4 ml) solvent. After 4 h of reaction, 56% isolated product of benzyl carbamate was obtained (Table 5, Entry 1). So this obtained result of catalysis reaction inspired us to optimize the reaction by varying solvents, temperature, time and catalyst loading. Table 5 represents the effect of solvents as well as temperature in the catalytic reaction. From table 5 it is clear that 1,4-dioxane is the most excellent solvent for the reaction (Table 5, Entry 4). Under solvent free condition we got only trace amount of desired product (Table 5, Entry 10). Then temperature optimization was examined. At room temperature only 24% of benzyl carbamate was appeared. With increasing reaction temperature the product yield was also improved and maximum product yield was observed at 80°C (Table 5, Entry 4). At 90°C temperature the product yield was reduced due to the formation of bicarbamate products (Table 5, Entry 14).

 Table 5. Effect of solvents and temperature in the catalysis reaction

Entry	Solvent	Temperature	Isolated yield of benzyl
		(°C)	carbamate (%)
1	MeCN	80	56
2	DCM	80	43
3	Benzene	80	68
4	1,4-Dioxane	80	88
5	DMF	80	71
6	DMSO	80	77
7	o-Xylene	80	73
8	Toluene	80	55
8	n-Bu <sub>2</sub> O	80	Trace
9	H <sub>2</sub> O	80	Trace
10	No solvent	80	Trace
11	1,4-Dioxane	r.t.	24
12	1,4-Dioxane	50	63
13	1,4-Dioxane	70	78
14	1,4-Dioxane	90	85

Reaction performed by taking benzyl amine (5 mmol), Urea (4 mmol), Cu-NPs@TzTa-POP catalyst (15 mg), 4 h.

After regulating the solvent and reaction temperature, we inspected the loading of catalyst on the same catalysis reaction (**Figure 11**). Without catalyst very trace amount of product was produced in 4 h of reaction.



 Fig. 11 Effects of catalyst loading on synthesis of benzyl carbamate from View Article Online benzyl amine and urea.
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By enhancing the catalyst loading, isolated yield of the product was also enhanced and highest yield of the product (98%) was attained by using 20 mg of catalyst. Utilization of 25 mg catalyst was not affecting the further increment of product yield.

The rate of the reaction with respect to time in presence and absence of Cu-NPs@TzTa-POP catalyst (Figure 12) was also observed under the optimized reaction conditions. From the figure it is clearly observable that the reaction was performed in faster rate and completed within 4 h in presence of catalyst but the reaction did not progress smoothly in absence of catalyst. After 6h of reaction, only 5% (approximately) yield of product was appeared.

Under optimized reaction conditions the catalytic reaction was carried out in presence of copper acetate salt (20 mg) and TzTa-POP (20 mg) as catalyst in two separate reactions. 36% isolated yield of benzyl carbamate was obtained in use of TzTa-POP support as catalyst whereas copper salt produced trace amount of product. The same reaction was performed in presence of our previously synthesized Cu-NPs@COF and its support (COF) as catalyst. Cu-NPs@COF synthesized 89% of desired product and COF produced 31% of the product. The summarized results for both catalytic reaction in presence of different catalysts and their supports definitely indicates the Synergistic Effect of support and copper nano particles.<sup>40</sup>



Fig. 12 Study of rate of benzyl carabamate formation in presence and absence of catalyst.

Therefore the catalytic formation of carbamates from various alcohols and urea was performed in presence of 20 mg Cu-NPs@TzTa-POP catalyst at 80°C in dioxane solvent. Both aromatic alcohols (benzyl alcohols and phenols) as well as aliphatic alcohols efficiently go through this catalytic reaction and produced moderate to high amount of corresponding product within 4 h of reaction (Table 6). The given data of each entry are the mean value of three successive reactions. The collected results of all reactions are given in Table S2. Benzyl alcohol and 4-methoxy benzyl alcohol (having electron donating group) gave very high yield of desired product (96.7%) in this catalytic reaction (Table 6, Entries 1,2) where as mild electron withdrawing group containing benzyl alcohol (such as 4-bromo benzyl alcohol) also gave very good amount of corresponding carbamate (91.7%) (Table 6, Entry 3). Strong electron withdrawing group containing benzyl alcohol (i.e. 4nitro benzyl alcohol) produced relatively lower (82.3%) of 4-nitro benzyl carbamate product (Table 6, Entry 4). Phenol and its derivatives (both electron donating and withdrawing group

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containing) were formed relatively less amount of carbamates product (56% to 77%) as compare to benzyl alcohols (Table 6, Entries 5-8). Phenylethyl alcohol gave 95.7% of corresponding desired product (Table 6, Entry 9). Then tolerance of different types of aliphatic alcohols (like propyl, isopropyl, butyl and pentyl alcohols etc.) were checked, all of them produced >88% yield of respective products (Table 6, Entries 11-14). Not only that, we also examined the efficiency of furan-2-ylmethanol (a hetero cyclic compound) in this catalytic reaction and got 72.7% isolated yield of Furan-2-ylmethyl carbamate (Table 6, Entry 10).

	·····,		
Entry	Alcohols	Carbamates	Isolated Yield (%)
1	ОН	NH <sub>2</sub>	96.7
	3a	4a	
2	Мео	NH <sub>2</sub>	96.7
		MeO	
	3b	4b	
3	OH OH	NH <sub>2</sub>	91.7
	Br		
	Зc		
4	ОН	,NH <sub>2</sub>	82.3
	0 <sub>2</sub> N-(_)		
		0 <sub>2</sub> N-()	
	3d	4d	
5	он		77.0
	3e	4e	
6	МеООН		81.7
		MeOONH <sub>2</sub>	
	3f	4f	
7	Ме-ОН		78.3
	3g	4g	
8	NO <sub>2</sub>	NO <sub>2</sub>	56.3
	он		
	3h	4h	
9	⊘Он		95.7
		0 <sup>-</sup> NH <sub>2</sub>	
	3i	4i	
10	ОН	0 II	72.7
		O NH <sub>2</sub>	
	3j	4j	
11	∕∕ОН	0 L	91.7
	3k	0 NH <sub>2</sub>	
12		4k	00 0
			00.3
	31	4	
13	ОН	NH <sub>2</sub>	93.7
	3m	4m	
	500		





"Reaction conditions: alcohols (5 mmol), urea (4 mmol), Cu-NPS@121a-POP catalyst (20 mg, 0.015 mmol based on copper metal), 1,4-dioxane (4 ml), 80°C, 4 h.

By the support of earlier reported publications<sup>28,31</sup> a plausible mechanism for the synthesis of primary carbamates from urea and alcohol is depicted in Scheme 5. Initially urea is activated by the catalyst through O-coordination to the copper centre of the catalyst (intermideate I). The electrophilic character of the carbonyl carbon is increased via this coordination.<sup>41</sup> Nucleophilic attacks of alcohol to the electron deficient carbonyl centre leads to the intermediate II.<sup>30b</sup> Transfer of a proton from alcohol to an amino group produces intermediate III. Then intermediate III gives rise to the final product after elimination of NH<sub>3</sub> molecule and regeneration of the catalyst.

#### Tests of heterogeneity for Cu-NPs@TzTa-POP catalyst

Hot filtration test in catalytic primary carbamates formation reaction was performed to check the heterogeneity nature of the Cu-NPs@TzTa-POP catalyst. Firstly, catalytic primary carabamates synthesis reaction from benzyl alcohol and urea was allowed to run under optimization reaction condition for 2h.



Scheme 5. Probable route of catalytic synthesis of primary carbamates from urea and alcohols.

After 2 h of reaction advancement, the catalyst was filtered out. The desired product yield was observed to be 57%. Then the residue reaction mixture was permitted to continue for another 2h without presence of Cu-NPs@TzTa-POP. It was found that the reaction did not make any progress without catalyst. AAS analyzation was done with the filtered catalyst and the filtrate reaction mixture. In filtrate, no trace amount of Cu metal was found. In recovered catalyst, same amount of copper metal loading (i.e. 4.86%) was arises as that of fresh catalyst. AAS analysis also been done with the catalyst after the first run of catalytic cycle. It showed no leaching of Cu metal. The recycled catalyst after 6<sup>th</sup> cycle was also analyzed by AAS method. It showed a negligible amount of metal leaching. For further confirmation of heterogeneity, FT-IR, XRD and XPS analysis were done with the recycled Cu-NPs@TzTa-POP catalyst. FT-IR and XRD data of the reused catalyst showed no significant change in peak position from the freshly prepared Cu-NPs@TzTa-POP (Figure S38, S39). In XPS analysis of recovered catalyst, no considerable alteration of peak position in the copper

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nanoaprticles was found (Figure 13). The characteristics binding energy peaks were observed at 932.1 eV, 951.9 eV which represents to Cu(0) Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$ , respectively and the peak difference (19.8 eV) is also same as that of synthesized catalyst. This result clearly confirms the unchanged oxidation state of copper nanoparticles in utilized catalyst.<sup>42</sup> All these analytical data clearly indicates the heterogeneity of Cu-NPs@TzTa-POP catalyst.

## Recyclability of Cu-NPs@TzTa-POP catalyst

The reusability and recyclability of Cu-NPs@TzTa-POP catalyst was screened for both catalytic reactions of N-methylation and primary carbamate formation reactions. After completion of every catalytic cycle, the catalyst was detached from the reaction mixture via simple filtration technique. Then recovered catalyst was washed properly with methanol and acetone for several times. After washing the catalyst, it was first air dried and then dried under vacuum. Next it was utilized for another catalytic cycle. Figure 14 evidently elucidates that Cu-NPs@TzTa-POP catalyst was sufficiently stable after subsequent employ of six cycles. Atomic absorption spectra analysis was performed to determine the copper amount present on TzTa-POP surface after six catalytic rounds, the result depicted that very negligible amount of copper metal was loosed from the surface. The recycled catalyst showed almost the same copper loading as that of fresh catalyst ( $\approx$ 4.78). Hence we can firmly conclude that Cu-NPs@TzTa-POP catalyst is heterogeneous catalyst which is easily recyclable and reusable.



Fig. 13 XPS spectra of used Cu-NPs@TzTa-POP catalyst for Cu 2P level.



Fig. 14 Graphical representation of recyclability test of Cu-NPs@TzTa-POP catalyst.

## Conclusion

designed heterogeneous copper nanoparticles A newly incorporated porous organic polymer (Cu-NPs@TzTa-POP) catalyst was synthesized and properly characterized by different instrumental methods. The low cost easily producible catalyst is very competent in the chemical fixing of atmospheric CO<sub>2</sub> in order to produce N-methylated compounds from aromatic and heterocyclic amines under moderate reaction conditions. Various N-methylated products were obtained up to 98% isolated yield with turnover frequency value from 18 to 42 h<sup>-1</sup>. Again the catalyst is also very proficient to manufacture primary carbamates from ecofriendly carbonylating agent urea and alcohols. Different benzylic alcohols, phenols, heterocyclic alcohols as well as aliphatic alcohols were very much tolerant to the catalytic reaction and produced moderate to high yield of respective carbamates under ambient conditions. Furthermore, outstanding catalyst recyclability and reusability are observed without substantial loss of active Cu metal, demonstrating the porous Cu-NPs@TzTa-POP material as a capable vibrant heterogeneous catalyst for both thermal catalytic reactions.

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59 60 **Keywords:** Heterogeneous catalyst, porous organic polymer, CO<sub>2</sub> fixation, N-methylation, Carbamates, Copper Nanoparticles.

### Conflicts of interest

There are no conflicts to declare.

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# **Graphical Abstract**

TriazineTriamine derived Porous Organic Polymer supported Copper Nanoparticles (Cu-NPs@TzTa-POP): An efficient catalyst for synthesis of N-methylated products via  $CO_2$  fixation and primary carbamates from alcohols and urea

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Copper nanoparticles incorporated TriazineTriamine derived Porous Organic Polymer-based catalyst was synthesized for catalytic production of N-methylated amines via CO<sub>2</sub> fixation reaction and primary carbamates formation from urea and alcohols.



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