# Nanoporous Copper Metal Catalyst in Click Chemistry: Nanoporosity-Dependent Activity without Supports and Bases

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**Abstract:** Nanoporous copper (CuNPore) catalysts with tunable nanoporosity were fabricated from  $Cu_{30}Mn_{70}$  alloy by controlling the de-alloying temperature under free corrosion conditions. The tunable nanoporosity of CuNPore led to a significant enhancement of catalytic activity in click chemistry without using any supports and bases. Characterization of CuNPore surface, high reusability, leaching experiment, and formation of nanostructured copper acetylide revealed that the click reaction occurred at the catalyst surface.

**Keywords:** click reaction; heterogeneous catalysis; high reusability; nanoporous copper catalyst; tunable nanoporosity

Nanoporous metals are promising materials for catalysis,<sup>[1-3]</sup> sensing,<sup>[4]</sup> and actuation<sup>[5]</sup> applications due to their interesting structural, optical and surface properties. In spite of the growing number of studies on various applications of nanoporous metals, the catalytic properties in chemical reactions are still less explored, although the interesting features of nanoporous metals make them potentially attractive candidates for new heterogeneous catalysts;<sup>[1-3]</sup> the three-dimensional, open-pore network structures and metal ligaments allow the transport of molecules and ions, a high surface-to-volume ratio in comparison with bulk metals results in outstanding catalytic efficiency; furthermore, the potentially high reusability and rather simple work-up are favorable for practical synthetic methodology. Moreover, in contrast to the supported nanoparticles (NPs) catalyst, a nanoporous metal without supports should be a challenging catalyst system to understand the relevant catalytic mechanism more easily and to extend the catalytic application widely by elimination of the support effect problems and relaxation of aggregation. In this regard, we have focused on the study of the catalytic properties of unsupported nanoporous metals in organic molecular transformations under liquid-phase conditions.<sup>[6]</sup> Nanoporous gold exhibited a remarkable catalytic efficiency and reusability in the oxidation of organosilanes into silanoles with water,<sup>[6a]</sup> and non-porous palladium without ligands and supports showed high catalytic activity and reusability in the Suzuki coupling.<sup>[6b]</sup> Therefore, the design and synthesis of new and efficient nanoporous metal catalytic systems for the development of molecular transformations are highly desirable.

In 2002, Sharpless<sup>[7a]</sup> and Meldal<sup>[7b]</sup> reported independently the Huisgen [3+2] cycloaddition of terminal alkynes and organic azides catalyzed by homogeneous Cu(I) salts, the so-called click reaction. This methodology has been emerged as the most powerful tool for connecting the two useful functional groups. During the last few years, numerous applications of the click reaction have been reported in the field of material sciences, bio- and medicinal chemistry.<sup>[8]</sup> The click reaction can be catalyzed also by heterogeneous copper(I), such as immobilized copper nanoclusters and copper/cuprous oxide NPs, copper-in-charcoal NPs, copper zeolites, and copper nitride NPs supported on mesoporous SiO<sub>2</sub> with or without bases.<sup>[9]</sup>

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lyze this click reaction, while the reaction is relatively slow and requires high catalyst loading.<sup>[10]</sup> Recyclability of these heterogeneous copper catalysts was rarely reported.<sup>[9i]</sup> Recently, it has been reported that the monolithic CuNPore is a promising high strength/low density material, which can be synthesized through the chemical or electrochemical de-alloying of various single-phase Cu/M (M=Al, Mg, Mn) alloys.<sup>[11]</sup> Herein, we report an efficient approach for the synthesis of CuNPore with tunable nanoporosity and its remarkable catalytic properties in click chemistry without using any supports and bases [Eq. (1)]. To the best of our knowledge, this is the first report on a monolithic CuNPore-catalyzed molecular transformation, while the non-monolithic CuNPore in the form of Raney copper is a well known catalyst in the water-gas shift reaction.<sup>[12]</sup>

$$R^{1} \longrightarrow R^{2} - N_{3} \xrightarrow{\text{cat. CuNPore}}_{\text{toluene or neat}} \xrightarrow{R^{1}}_{N \\ N \\ 65 \ ^{\circ}\text{C}} \xrightarrow{N}_{3} (1)$$

Initially, we attempted to fabricate uniform CuN-Pore catalysts having different ligament diameters because it has been proved that the tunable size and shape of nanostructured materials may provide various physical and chemical properties.<sup>[11d,13]</sup> To date, less attention has been paid to the synthesis of CuN-Pore with a tunable nanoporosity by changing the dealloying conditions. Recently, Chen and co-workers obtained CuNPores with tunable nanopore sizes from Cu/Mn ribbons by controlling de-alloying time and electrolyte concentration under an electrochemical method.<sup>[11e]</sup> However, the small thickness (~20 µm) and width (~1 mm) of the used ribbon would be brittle during the catalytic transformations. After screening a number of de-alloying conditions, we fabricated CuNPore catalysts with tunable nanoporosity by changing the de-alloying temperature under a modified Hayes method;<sup>[11a]</sup> free corrosion of a homogeneous  $Cu_{30}Mn_{70}$  alloy with a thickness of ~200 µm and size of  $\sim 5 \times 5$  mm by using (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (1M) and MnSO<sub>4</sub> (0.01 M) as electrolytes [see Figure S1 in Supporting Information]. Scanning electron microscopy (SEM) images in Figure 1 (a)-(e) showed that ligaments and nanopore channels were formed uniformly across the entire CuNPore. The average ligament diameters of CuNPore were estimated as ~25 nm (0°C, cat-1), ~30 nm (10°C, cat-2), ~40 nm (25°C, cat-3), ~50 nm (40 °C, cat-4), ~70 nm (60 °C, cat-5) (Table 1). Energy dispersive X-ray (EDX) studies showed that the residual manganese composition of CuNPore for the 0  $^{\circ}$ C de-alloyed sample (cat-1) is ~4 at%, and remains approximately constant at ~2 at% for cat-2 to cat-5 (Supporting Information, Figure S2).

The catalytic activities of various fabricated CuN-Pore materials were examined in the click reaction of phenylacetylene (1a) and benzyl azide (2a) in toluene at 65 °C for 2 h without using any supports and bases (Table 1). The reactions using CuNPore catalysts with ligament sizes of about ~25 nm and ~30 nm (cat-1 and cat-2) gave moderate yields of the corresponding triazole 3a (entries 1 and 2). Surprisingly, the use of cat-3 having a ligament size about ~40 nm afforded 3a in almost quantitative yield (entry 3). The specific surface area of cat-3 was measured by the BET



**Figure 1.** SEM images of CuNPore fabricated by de-alloying of  $Cu_{30}Mn_{70}$  in 1 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and 0.01 M MnSO<sub>4</sub> at (**a**) 0°C (6 days, cat-1), (**b**) 10°C (6 days, cat-2), (**c**) 25°C (6 days, cat-3), (**d**) 40°C (4 days, cat-4), (**e**) 60°C (4 days, cat-5); (**f**) SEM image of nanostructured copper acetylide.

Table 1. Screening of copper catalysts.<sup>[a]</sup>

Ph —=== 1a	+ Dr N	Cu catalyst ( 2 mo	I%) Ph	
	- Bn−N <sub>3</sub> 2a	toluene 65 °C, 2 h	→ / / / N · Br N N · Br 3a	
Entry	Cu catalyst (ligament size)		Yield of <b>3a</b> [%] <sup>[b]</sup>	
1	CuNPore (	cat-1, ~25 nm)	42	
2	CuNPore (	cat-2, ~30 nm)	51	
3	CuNPore (	cat-3, ~40  nm	99 <sup>[c]</sup>	
4	CuNPore (	cat-4, ~50  nm	69	
5	CuNPore (	cat-5, ~70 nm)	48	
6	$Cu_{30}Mn_{70}$ al	lov	0	
7	Cu <sub>2</sub> O		3	
8	CuO		3	

<sup>[a]</sup> The reaction of **1a** and **2a** (1 equiv.) was carried out in the presence of 2 mol% of Cu catalyst in toluene (2M) at 65 °C for 2 h.

 $^{[b]}$   $^1H\,NMR$  yield determined using  $CH_2Br_2$  as an internal standard.

<sup>[c]</sup> Isolated yield.

method to be  $14 \text{ m}^2\text{g}^{-1}$ , the turnover frequency (TOF) thus reached to  $0.26 \text{ s}^{-1}$ . It should be noticed that the reaction can be catalyzed by cat-3 at ambient temperature, although it required a longer reaction time (30 h). The reaction using cat-4 or cat-5 having ligament sizes larger than cat-3, resulted in a dramatically decreased yield of **3a** (entries 4 and 5). Cu-Mn alloy was totally inactive as a catalyst (entry 6). These results indicate that the tunable nanoporosity of CuN-Pore has a strong influence on catalytic activity in the click reaction. The remarkable difference in catalytic activities cannot simply be attributed to the difference in surface areas, because the CuNPore catalyst with a ligament size smaller than 40 nm exhibited a lower catalytic activity. A similar effect of nanopore size was observed in CuNPore-based surface-enhanced Raman scattering (SERS); CuNPore with nanopore sizes about 30-50 nm significantly enhanced SERS intensity while a dramatic loss of the SERS effect was observed for nanopore sizes larger or smaller than that.<sup>[11e]</sup>

A number of homogeneous and heterogeneous examples proved that the click reaction was catalyzed by Cu(I) species.<sup>[7–9]</sup> X-ray photoelectron spectroscopy (XPS) spectra showed that the fresh CuNPore surface is composed of Cu(0), Cu(I), and Cu(II) species, while Cu(I) is a predominant component (Supporting Information, Figure S4).<sup>[14]</sup> The Cu 2*p* peaks at 932 eV and 953 eV and Cu LMM Auger peak at 568 eV were assigned to Cu(0); peaks at 570 eV, 932 eV, and 953 eV were ascribed to Cu(I); several satellite peaks at 935 eV, 944 eV, 955 eV, and 963 eV correspond to Cu(II). The Cu(I) and Cu(II) ions exist as the native Cu<sub>2</sub>O and CuO on CuNPore surface.

The XPS spectra of cat-1 to cat-5 having different ligament sizes did not show a significant difference on the surface component (Supporting Information, Figure S3). Moreover, after reaction, the satellite peaks of Cu(II) were almost disappeared while Cu(I) remained predominantly (Supporting Information, Figure S4). This result suggested that some amounts of Cu metal might be leached to the organic solvent. Indeed, the inductively coupled plasma (ICP-AES) analysis showed that only 0.2 ppm of Cu was leached after reaction. To clarify whether the leached Cu metal catalyzes the present reaction or not, we monitored the reaction with or without catalyst. The reaction of **1a** and **2a** was carried out by using 5 mol% of cat-3 in toluene (0.5M) at 65°C. After 3 h, CuNPore catalyst was removed from the reaction vessel and 3a was produced in 38% <sup>1</sup>H NMR yield at this time [Figure 2, (a),  $\blacksquare$  symbols]. The reaction mixture was continuously heated in the absence of the catalyst for 1 h, affording **3a** in 40% yield, while the reaction was completely stopped in the next 1 h. The reaction restarted when cat-3 was put back into the mixture and finally gave 3a in 99% yield within 4 h. On the other hand, the control reaction without removal of catalyst was complete in 6 h, giving **3a** in 98% yield [Figure 2, (a) ● symbols]. These results indicated that the leached copper was mainly Cu(II) species which was unable to catalyze the present click reaction, suggesting that the reaction is catalyzed by Cu(I) ions on the CuNPore surface. It should be noted that Cu<sub>2</sub>O or CuO powder cannot catalyze this reaction without a base (Table 1, entries 7 and 8). These results further support that the nanoporous structure plays a crucial role in the current catalysis.

The CuNPore (cat-3) catalyst was reused for multiple cycles without significant loss of catalytic activity in the reaction of **1a** and **2a**; the yield was still 98% in the tenth cycle [Figure 2, (**b**)]. After simple filtration of the reaction mixture, the catalyst was washed with acetone and reused without further purification. The product was produced almost quantitatively in every



Figure 2. (a) Leaching test of CuNPore for the reaction 1a with 2a was performed by using 5 mol% of cat-3 in toluene (0.5 M) at 65 °C. (b) Reusability study of CuNPore (cat-3) for the reaction of 1a with 2a was carried out in toluene (0.5 M) at 65 °C for 6 h.

cycle and the turnover number (TON) reached up to 8200. It is noteworthy that the nanostructure of the recovered catalyst did not show significant changes after the fifth cycle, however, the nanostructure on surface was not clear after the tenth cycle while the cross-sectional nanostructure survived well (Supporting Information, Figure S5).

Involvement of copper(I) acetylide species in the click reaction is well demonstrated by computational study and kinetic experiments.<sup>[15,16]</sup> During this study of the catalytic properties of CuNPore materials, we found that when cat-3 was treated with an excess amount of phenylacetylene in toluene without organic azides at room temperature, the CuNPore catalyst surface was turned to vellow after washing with acetone and dichloromethane. The SEM image showed that the cat-3 surface was covered with a uniform grass-like material [Figure 1, (f) and Supporting Information, Figure S6]. A binding energy peak appeared in between those of CuO and Cu<sub>2</sub>O, and peaks of Cu(II) and Cu(0) were not detected in the XPS spectra, suggesting that the new peaks (marked by \*) of the grass-like material surface should be assigned to Cu(I) species (Supporting Information, Figure S7). However, treatment of cat-3 with benzyl azide without phenylacetylene did not change the nanoporous structure of the catalyst. These results prompted us to examine the possibility of the nanostructured copper acetylide formation. When the grass-like material [shown in Figure 1, (f)] was treated with benzyl azide at 65°C for 2 h, the grass-like material disappeared from the surface, the nanoporous structure of cat-3 was recovered, and a very small amount of the corresponding triazole **3a** was detected by <sup>1</sup>H NMR and GC-MS. Moreover, the recovered CuNPore retained its high catalytic activity in the reaction of 1a and 2a (99% of **3a**), although the reaction with the grass-like material as a catalyst gave 58% of 3a. These results implied that the grass-like material should be the nanostructured *polymeric* copper acetylide which was less active than the copper acetylides with lower order aggregates generated in situ. The results were in good agreement with the previous DFT studies and experimental investigation reported by Fokin<sup>[15]</sup> and Straub.<sup>[16]</sup> It is noteworthy that the nanostructured copper acetylide was very stable in air compared to the air-sensitive fresh CuNPore, suggesting that the polymeric copper acetylide can be used as a CuNPore metal storage to protect the nanoporosity of CuNPore from air.

The catalytic activity of CuNPore (2 mol% cat-3) was further examined with various terminal alkynes and organic azides in toluene (2 M) at 65 °C (Table 2). Not only aromatic and heteroaromatic alkynes but also alkylalkynes were catalyzed regioselectively, affording 1,2,3-triazoles in excellent yields (entries 1–7). Various functional groups, such as alkene, ester, and

**Table 2.** CuNPore (cat-3)-catalyzed synthesis of various substituted triazoles.<sup>[a]</sup>

R <sup>1</sup> −≡	$\equiv$ + R <sup>2</sup> -N <sub>3</sub>	2 mol% cat-3		$\mathbb{R}^{1}$
		toluene (2 M)	), 65 °C	N N R <sup>2</sup>
1	2			3
Entry	$\mathbf{R}^{1}$ 1	$\mathbf{R}^2 2$	Time [h]	Yield [%] <sup>[b]</sup>
1	2-pyridyl <b>1b</b>	Bn <b>2a</b>	4.5	<b>3b</b> , 96
2	3-thienyl 1c	Bn <b>2a</b>	7	<b>3c</b> , 99
3	<i>n</i> -pentyl <b>1d</b>	Bn <b>2a</b>	6	<b>3d</b> , 99
4	c-hexyl 1e	Bn <b>2a</b>	4	<b>3e</b> , 97
5	<i>t</i> -Bu <b>1f</b>	Bn <b>2a</b>	22	<b>3f</b> , 99
6	$HOCH_2$ 1g	Bn <b>2a</b>	19	<b>3g</b> , 94
7 <sup>[c]</sup>	Ph <b>1a</b>	Ph <b>2b</b>	22	<b>3h</b> , 95
8 <sup>[c]</sup>	Ph <b>1a</b>	cinnamyl 2c	19	<b>3i</b> , 99
9	Ph <b>1a</b>	$EtO_2CCH_2$ 2d	3	<b>3j</b> , 99
10	BnNHCH <sub>2</sub> 1h	Ph <b>2b</b>	3.5	<b>3k</b> , 95
$11^{[d]}$	TsNHCH <sub>2</sub> 1i	Ph <b>2b</b>	6	<b>3l</b> , 98

[a] Reaction conditions: to a toluene (2M) solution of cat-3 (2 mol%) was added alkyne 1 and azide 2 (1 equiv.). The mixture was stirred at 65 °C for the time shown in Table 2.

<sup>[b]</sup> Isolated yield.

<sup>[c]</sup> 2 equiv. azide were used.

<sup>[d]</sup> 1.2 equiv. azide were used.

protected amines were tolerated under the present heterogeneous conditions (entries 8–11). Under neat conditions, the catalytic loading can be decreased to 0.1 mol% without any significant influence on the reaction efficiency, and the TOF was increased up to  $5.2 \text{ s}^{-1}$  [Eq. (2)].

$$R^{1} \longrightarrow H = Bn - N_{3} \xrightarrow{0.1 \text{ mol}\% \text{ cat-3}}_{\text{neat, 65 °C}} \longrightarrow N_{N - R^{2}}^{R^{1}} (2)$$
**1a** R<sup>1</sup> = Ph **2a 3a** 99% (2 h)  
**1e** R<sup>1</sup> = *c*-hexyl **3e** 95% (4 h)

In conclusion, we have developed an efficient approach for the fabrication of nanoporous copper materials with tunable nanoporosity, and demonstrated that CuNPore has an outstanding catalytic activity for click chemistry without using any supports and bases. The catalytic activity was highly in dependence on the ligament (or pore) sizes of the CuNPore materials; ligament size about ~40 nm significantly enhanced the catalytic efficiency. Characterization of the catalyst surface, leaching experiments, and the formation of nanostructured copper acetylide revealed that the present click reaction is catalyzed by Cu(I) species on the CuNPore surface. The CuNPore catalyst exhibited a high reusability; it can be recycled for ten times without significant loss of activity. A wide range of al-

kynes and azides can be tolerated, giving the corresponding triazoles in excellent yields. Further studies on exploring new catalytic activities of CuNPore materials and extension of its utility to organic synthesis are in progress.

## **Experimental Section**

#### **Representative Fabrication Method of Nanoporous Copper (cat-3)**

The rolled alloy  $Cu_{30}Mn_{70}$  with 200 µm thickness and 5 mm × 5 mm size was placed directly in 1M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and 0.01 M MnSO<sub>4</sub> electrolytes at room temperature (25 °C) for 6 days. All electrolytes were prepared with deionized (DI) water and reagent grade chemicals. After de-alloying, the sample was removed from electrolytes and rinsed in DI water for few minutes. The sample was then washed with acetone and dried under vacuum. The dried CuNPore was stored in a glove box. Using the same electrolytes, cat-1 and cat-2 were fabricated at 0°C and 10°C for 6 days, respectively. Cat-4 and cat-5 were de-alloyed at 40°C and 60°C for 4 days.

#### **Representative Procedure for the CuNPore (cat-3)-Catalyzed Click Reaction**

To a toluene (2M, 0.5 mL) solution of CuNPore (cat-3, 2 mol%, 1.3 mg) were added phenylacetylene **1a** (1 mmol, 112  $\mu$ L) and benzyl azide **2a** (1 mmol, 125  $\mu$ L) in a V-shaped reactor vial. The reaction mixture was stirred at 65 °C for 2 h by using a bulky round-shaped magnetic stirring bar. After consumption of **1a** and **2a** which were monitored by TLC, the reaction mixture was cooled to room temperature. The mixture was filtered and washed with dichloromethane. The recovered CuNPore catalyst was washed with acetone and dried under vacuum. After concentration of the filtrate, the white solid was purified via short silica gel chromatography by using a 3:1 mixture of hexane and ethyl acetate as an eluent, to afford 1-benzyl-4-phenyl-1*H*-1,2,3-triazole **3a** as a white solid; yield:233 mg (99%).

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