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A Facile Synthesis of Copper Nanoparticles Supported on Ordered Mesoporous Polymer as an Efficient and Stable Catalyst for Solvent-Free Sonogashira Coupling Reactions

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Abstract

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A novel mesoporous phenol-formaldehyde resin supported copper nanoparticles was prepared by using a two-step protocol involved the melt infiltration of copper nitrate hydrates and the subsequent template pyrolysis-induced in-situ reduction of Cu(II) ions. Notably, this synthetic process effectively saved time and reduced wastes since it didn't use any solvents, capping and reducing reagents. The obtained Cu NPs@MP catalysts had the large surface areas and narrow pore size distributions. In addition, most of the Cu nanoparticles with the sizes around 3-5 nm were highly dispersed in the pore channels of mesoporous polymers. In the solvent-free Sonogashira reactions for the synthesis of ynones from acyl chlorides and terminal alkynes, it exhibited much higher catalytic reactivity than those of the commercial Cu powder and mesoporous silica SBA-15 supported Cu nanoparticles. The excellent catalytic performance could to the synergistic advantages of mesoporous be attributed structure. monodispersed Cu nanoparticles and the surface hydrophobicity, which stabilized and concentrated the reactants and increased the accessibility of active sites as well as decreased the mass transfer resistance. Meanwhile, it could be easily recycled and reused for at least ten times, showing a good stability under solvent-free reaction conditions.

Introduction

economic consideration and environmental concern, Driven by the replacement of expensive precious metals by cheap and earth-abundant base metals as the novel catalytic materials is one of major goals of s chemistry.¹ In this context, base-metal nanoparticles are among the very important catalytic components because of the high accessible surface area and unique quantum effect.² Among various base-metal nanopaticles, copper nanoparticles (Cu NPs) display the unique catalytic reactivity in a wide range of chemical synthesis and energy related fields such as azide-alkyne cycloaddition,³ hydrogenation,⁴ reduction,⁵ oxidation⁶ and cross-coupling reactions⁷. Generally, Cu NPs with small sizes are preferred since the particle size that less than 10 nm with a narrow size distribution is believed to be most beneficial for their catalytic efficiencies.⁸ However, the increased surface energy with the decreased particle size inevitably causes the serious aggregation, thereby leading to the inferior performances in the practical applications.⁹ A straightforward strategy to solve this problem is using the support materials to disperse and fix the Cu NPs.¹⁰ Accordingly, the catalytic properties of the supported Cu NPs catalysts strongly depend on the preparation method.¹¹ To date, the impregnation, drying and the subsequent reduction procedures with Cu metal salts as the precursors is the most widely applied protocol for the preparation of supported Cu NPs catalysts.¹² Unfortunately, these composites were often obtained with inhomogeneous nanoparticle size and dispersion after different reduction

processes.¹³ For this reason, the additional capping agents were frequently used to overcome this drawback.¹⁴ Obviously, this traditional multi-step operation with the certain amounts of capping and reducing agents and massive solvents is not a green and convenient process, which usually generates useless byproducts and wastes time. Therefore, there is a critical need to develop a simple, economical and environmentally friendly strategy for the preparation of the efficient and stable solid-supported Cu NPs catalyst.

Recently, melt infiltration is considered as the novel promising technique for the fabrication of nanoporous materials supported catalysts.¹⁵ It allows metal salts to permeate into a porous support via capillary force without the addition of any solvents and capping agents. This unique feature is of particular interest for the fabrication of metal nanoparticles-incorporated mesoporous materials with the high surface area and uniform pore size distribution. Specifically, this simple preparation procedure avoids the redistribution of the precursor phase during solvent removal.¹⁶ Moreover, the confined nanoscale channels of mesoporous materials inhibit the tendency of metal nanoparticles to grow into the larger crystallites through migration and coalescence of particles.¹⁷ The synergistic effects from both the preparation method and the supports are expected to provide excellent activity and selectivity superior to what can be obtained from the traditional solid supported metal nanoparticles. Up to now, the utilization of melt infiltration strategy for the preparation of mesoporous materials-support metal nanoparticles is very rare. Moreover, in these previously reported

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examples, a necessary post-treatment to reduce the metal salts to metal^oparticles³³ in the high temperature is an important cause for unwanted sintering of the supported metal active species.¹⁸

Mesoporous polymers have attracted enormous interest for the design of novel heterogeneous catalysts owing to their combined advantages of mesoporous materials and organic polymers including large surface area, tunable pore structure, high hydrophobicity and excellent stability in acid or base media.¹⁹ Due to these distinctive properties, several different mesoporous polymer supported metal nanoparticles have shown the enhanced catalytic performances in comparison to mesoporous silica-based catalysts.²⁰ However, to our knowledge, the use of melt infiltration strategy for the green synthesis of mesoporous polymer supported Cu NPs catalyst has not been reported so far. Herein, for the first time, we demonstrated a facile capping and reducing agents-free and solvent-free strategy for dispersing copper nanoparticles in the channels of mesoporous phenol-formaldehyde polymer by a convenient two-step protocol involved the melt infiltration of copper nitrate hydrates and the subsequent template pyrolysis-induced in-situ reduction. The obtained composite possessed high surface area, ordered mesoporous structure and monodispersed Cu nanoparticles in the mesoporous channels with the size of about 3-5 nm. Notably, this heterogeneous Cu catalyst exhibited excellent catalytic activity and selectivity towards solvent-free synthesis of a variety of ynones from acyl chlorides and terminal alkynes. Meanwhile, it could be easily reused and

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recycled for at least 10 times without the loss of the activity, showing a good³ potential in the future industrial application.

Experimental Section

1. Sample Preparation

1.1 Synthesis of phenol-formaldehyde polymer with F127 template composite (PF). Firstly, phenol-formaldehyde polymer with F127 template composite was synthesized via evaporation-driven self-assembly method. In a typical procedure, 1.0 g phenol and 0.21 g aqueous NaOH solution (20 wt.%) were mixed and stirred at 40°C for 0.5 h. Then, 1.72 g aqueous formaldehyde solution (37 wt.%) was added dropwise into the mixture and continued to stir at 70°C for 2.0 h. After the mixture was cooled down to room temperature, the pH value was adjusted to 7.0 by adding a certain amount of aqueous HCl solution (2.0 mol/L). Next, the phenol-formaldehyde resol oligomers were obtained after removing water by rotary evaporation. The oligomers were then dissolved in ethanol to remove NaCl precipitate. Subsequently, 5.0 g the as-prepared oligomers ethanol solution (20 wt.%) was added into 20 g ethanol solution containing 1.0 g triblock copolymer Pluronic F127 template (EO₁₀₆PO₇₀EO₁₀₆). After stirring for 10 min, the mixture was transferred into the dishes for evaporation at 25°C for 12 h and further thermopolymerized at 100°C for 24 h. The final powder sample was scratched from the dishes and vacuum dried at 80°C for 10 h.

1.2 Preparation of ordered mesoporous polymer supported copper nanoparticles

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catalyst (Cu NPs@MP). This novel catalyst was prepared by two-step solid-state ball milling and *in-situ* pyrolyzed reduction procedures. Typically, a certain $Cu(NO_3)_2 \cdot 3H_2O$ mixed with as-synthesized amount of was 1.0 g phenol-formaldehyde polymer with F127 template composite powder by the ball milling for 12 h at 25°C. Then, this composite was transferred into quartz boat and then pyrolyzed in N_2 atmosphere at 350°C for 6.0 h with a heating rate of 2.0 °C/min. The obtained samples were denoted by the mass loadings of $Cu(NO_3)_2 \cdot 3H_2O$ in the initial mixture. Specifically, Cu NPs@MP-1, Cu NPs@MP-2, Cu NPs@MP-3 and Cu NPs@MP-4 samples were prepared according to the use of 50 mg, 75 mg, 100 mg and 125 mg $Cu(NO_3)_2 \cdot 3H_2O_2$, respectively.

1.3 Synthesis of ordered mesoporous silica supported copper nanoparticles (Cu NPs@SBA-15). Mesoporous silica SBA-15 was synthesized according to the method reported by Zhao group.^{21a} Then, 100 mg Cu(NO₃)₂·3H₂O was mixed with 1.0 g as-synthesized silica with P123 template by the ball milling for 12 h at 25°C. Then, this sample was transferred into quartz boat and then pyrolyzed in N₂ atmosphere at 350°C for 6.0 h with a heating rate of 2.0 °C/min, resulting in the final Cu NPs@SBA-15 sample.

1.4 Synthesis of hydrophobic ordered mesoporous silica supported copper nanoparticles (Cu NPs@TMS-SBA-15). 1.0 g as-prepared Cu NPs@SBA-15 was firstly dispersed in 50 ml toluene under N_2 atmosphere.^{21b} Then, 3.0 ml ethoxytrimethylsilane (TMS-silane) was added dropwise into the above solution

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and allowed to stir for 12 h under reflux condition. The powder^oproduct^Gwas³⁰ filtered and washed thoroughly with absolute toluene to eliminate un-reacted TMS-silane, followed by vacuum drying at 80°C for 12 h.

2. Characterization.

The copper loadings were determined on an inductively coupled plasma optical emission spectrometer (ICP-OES, Varian VISTAMPX). The copper electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ESCA). All the binding energy values were calibrated by using C1s = 284.6 eV as a reference. Fourier transform infrared (FTIR) spectra were obtained using Thermo Nicolet Magna 550 spectrometer. UV-visible spectroscopy (UV-vis) was obtained on Shimadzu MC-2530 spectrometer. Thermogravimetric-mass spectrometric (TG-MS) data was received on a Setaram TGA92 analyzer at a 2.0 °C/min heating rate in an inert helium atmosphere. X-ray diffraction (XRD) patterns were obtained on a Rigaku D/maxr B diffractometer with Cu K α radiation. N₂ adsorption-desorption isotherms were measured at 77 K with a Micromeritics TriStar II 3020 analyzer. Transmission electron microscope images were acquired on a JEOL JEM2011 microscope. Toluene and Water vapour absorption tests were carried out on an intelligent gravimetric analyse (Hiden Isochema IGA-002/3) by adding a dosed amount of high-purity vapor directly into the sample chamber and recording the weight change after stable equilibrium pressure was reached.

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3. Activity test

In a typical run of solvent-free Sonogashira coupling reaction, 0.50 mmol phenylacetylene, 1.5 mmol benzoyl chloride, 1.5 mmol triethylamine and 1.0 mol% Cu NPs@MP catalyst were mixed in a 25 ml oven-dried reaction tube. After reacting in nitrogen atmosphere at 40°C for 8.0 h, the reaction mixture was filtrated and then extracted with toluene, followed by analyzing on a high-performance liquid chromatography with mass spectrometry (HPLC/MS, Agilent 6410B). The reproducibility was checked by repeating experiments at least three times and was found to be within acceptable limits (±5%).

In order to determine the recyclability of Cu NPs@MP-3 catalyst, it was allowed to settle down after each run of reactions and the clear supernatant liquid was decanted slowly. The residual solid catalyst was washed thoroughly by toluene and re-used with a fresh charge of the reactants for subsequent recycling under the same reaction conditions. The content of copper leached off from the heterogeneous catalyst was also calculated by ICP analysis.

Results and discussion

The preparation protocol of the series of Cu NPs@MP samples was illustrated in Scheme 1. Phenol-formaldehyde polymer with F127 template composite (PF) was firstly synthesized according to the previously reported approach. Next, a certain amount of copper nitrate hydrate was infiltrated into the confined place between polymer wall and F127 template *via* a simple ball milling treatment. The obtained copper salt containing polymer composite (Cu(II)@PF) was further pyrolyzed in N₂ atmosphere to remove F127 template and simultaneously the pyrolysis-generated reducing gas *in-situ* reduced Cu(II) species to metallic Cu(0) in the pore channels of ordered mesoporous polymer, resulting in ordered mesoporous phenol-formaldehyde polymer supported copper nanoparticles materials (Cu NPs@MP).



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Scheme 1 Schematic illustration of the synthesis of ordered mesoporous polymer supported Cu NPs catalyst (Cu NPs@MP).

Inductively coupled plasma (ICP) analysis revealed that the copper content in the series of Cu NPs@MP samples was varied from 2.95 to 6.87 wt.%, confirming the existence of copper species (Table 1). Furthermore, X-ray photoelectron spectroscopy (XPS) spectra of the representative Cu NPs@MP-3 sample (Figure 1) indicated that the peaks at 932.9 and 952.7 eV correspond to $2p_{3/2}$ and $2p_{1/2}$ binding energies of zero-valent copper.²² Meanwhile, UV-Vis spectrum of Cu NPs@MP-3 (Figure 2) exhibited the remarkable broad absorption in the visible region (400-700 nm) in comparison with

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Sample	Cu (wt %)	$S_{BET} \left(m^2 / g \right)$	Dp (nm)	Vp (cm $^{3}/g$)
Cu NPs@MP-1	2.95	464	4.6	0.41
Cu NPs@MP-2	4.37	426	4.4	0.38
Cu NPs@MP-3	5.66	391	4.3	0.35
Cu NPs@MP-4	6.87	367	4.1	0.33
Cu NPs@SBA-15	5.43	565	5.2	0.60
Cu NPs@TMS-SBA-15	5.64	370	4.2	0.41
Cu NPs@MP-3 ^a	5.65	306	3.1	0.22

Table 1 Cu loadings and textural parameters of different Cu-containing catalysts.

^a after ten repetitions.

Cu(NO₃)₂·3H₂O precursor, which could be ascribed to the plasmon resonance bands of Cu nanoparticles.²³ These results clearly demonstrated the successful incorporation of metallic Cu(0) species in the phenol-formaldehyde polymer. To explore the unique redox reaction in our preparation process, we firstly analyzed the electric state of Cu species in Cu(II)@PF-3 by XPS analysis (Figure 1). The results showed that the measured binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ in Cu(II)@PF-3 were 935.3 and 955.2 eV, respectively, which indicated that Cu

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Figure 1 Cu 2p XPS spectra of Cu(II)@PF-3 and Cu NPs@MP samples.

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Figure 2 UV-Vis spectra of $Cu(NO_3)_2 \cdot 3H_2O$, Cu(II)@PF-3 and Cu NPs@MP samples.



Figure 3 TG-MS spectra of Cu(II)@PF-3 sample.

species were present in divalent state. Furthermore, two shake-up lines located at 944.1 and 963.0 eV were observed, which was indicative of the paramagnetic chemical state of $Cu^{2+,22}$ Also, UV-Vis spectrum of Cu(II)@PF-3 only showed the existence of absorption peak from 250-450 nm, which was derived from the aromatic framework of the polymer. On basis of these data, we suggested that the ball-milling treatment didn't reduce Cu(II) salt to Cu nanoparticles and the thermal pyrolysis caused Cu(II) ions to Cu nanoparticles. Next, we used TG-MS analysis to confirm this valence state transformation.^{24a} As shown in Figure 3, the thermogravimetric plot of Cu(II)@PF-3 sample presented one major weight loss from 280 to 380 °C. The coupled TG-MS analysis reveals that the very rich spectrum that contained several mass fragments was observed. The species with m/z = 16, 28, 42 and 56 could be probably assigned to methane, carbon monoxide, propene from the hydrophobic part of the polyalkeneoxide and the oligomer fragments, respectively.^{24b} These results confirmed that the reduction

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from Cu(II) ions to Cu nanoparticle was due to the existence of these reducing^{view Article Online} species in the pyrolysis treatment. Meanwhile, this process also generated a large amounts pore due to the removal of F127 template.



Figure 4 N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of different Cu NPs@MP catalysts.

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 N_2 sorption-desorption isotherms (Figure 4a) of all the Cu NPs@MP samples displayed the representative type IV curves with pronounced H₂ hysteresis loops and large uptakes at the relative pressure at p/p₀=0.45-0.70, which demonstrated that these samples had a mesoporous structure.²⁵ Their pore size distribution curves from the adsorption branches by using BJH model (Figure 4b) confirmed the presence of relatively uniform mesopores in these materials. According to the N_2 isotherms, the textural parameters were summarized in Table 1. These mesoporous Cu NPs-containing polymers had high surface areas (367-464 m²/g) and large pore volumes (0.33-0.41 cm³/g). The mean mesopore sizes of the

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samples ranged from 4.1-4.6 nm, slightly declining with the increase loading of Cu NPs, which was due to the occupation of the pore channels by the Cu NPs.²⁶



Figure 5 Small-angle XRD patterns (a) and wide-angle XRD patterns (b) of different Cu NPs@MP catalysts.

Small-angle XRD pattern (Figure 5a) of the pristine mesoporous phenol-formaldehyde resin (MP) exhibited one intense peak indicative of (100) reflection and two weak peaks assigned to (110) and (200) reflections in the enlarged inset picture, confirming the ordered 2-dimensional hexagonal mesostructure (*p6mm*). After the immobilization of Cu NPs, these Cu NPs@MP samples also displayed one peak indexed to the (100) diffraction, which confirmed the mesoporous structures were preserved.²⁷ The disappearance of (110) and (200) diffractions in these samples indicated the decreased order degree in comparison with the pristine mesoporous phenol-formaldehyde resin. Meanwhile, the peak intensities of (100) diffraction peak were gradually

decreased with the increase amounts of Cu(II) salt in a series of $Cu^{0}NPSOMP^{3}$ samples, which implied that the introduction of Cu NPs might slightly disturb the ordered structure of mesoporous polymer. The (100) peak shifted to the higher 20 values with the increase amounts of Cu NPs, which was maybe due to the increase in the pore thickness.²⁸



Figure 6 TEM images and particle size distributions (inset) of Cu NPs@MP-1 (a), Cu NPs@MP-2 (b), Cu NPs@MP-3 (c), Cu NPs@MP-4 (d) samples.

Furthermore, the Cu nanoparticles diameter and size distribution of these four Cu NPs@MP materials were analyzed by TEM images (Figure 6). The results revealed that the typical two-dimensional hexagonal arrangements of one-dimensional channels with uniform sizes were observed in large domains for

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all the samples. Meanwhile, TEM images showed that the small metal³ nanoparticles were well-dispersed inside the channels without the obvious aggregation, even for Cu NPs@MP-3 with 5.6 wt.% loading. Next, the respective particle size distributions of these Cu NPs@MP samples were obtained by counting the sizes of a certain amounts of Cu NPs. The result revealed that the dispersions of Cu NPs were related to their particle loadings. With the increasing Cu NP loadings, the particle sizes increased accordingly and meanwhile the particle dispersion was becoming broader. Accordingly, the particle size distribution of Cu NPs@MP-1 was in the range of 3.5-4.5 nm while the particle size distribution of Cu NPs@MP-4 was around 4.0-5.5 nm. But, the particle sizes of most of the Cu NPs were smaller than the pore sizes of the Cu NPs@MP samples, indicating that most of the nanoparticles were existed in the mesopore channels. Moreover, wide-angle XRD patterns (Figure 5b) exhibited that no obvious characteristic peaks of Cu NPs were obtained in the Cu NPs@MP-1 and Cu NPs@MP-2, which was maybe due to the Cu nanoparticles with the relative low loadings were highly dispersed in the mesoporous polymer. But, the peak around $2\theta = 43.3^{\circ}$ corresponding to (111) crystal plane was observed in Cu NPs@MP-3. Also, Cu NPs@MP-4 showed two pattern peaks at 43.3° and 50.3° , which could be assigned to the crystal planes of (111) and (200), respectively.²⁹ This phenomenon was related to the large particle size and the slight particle aggregation in Cu NPs@MP-4, in accordance with TEM result.

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Entry	Sample	Cu loading (wt.%)	Yield (%)	TON ^d
1^{b}	Blank	/	0	0
2	Cu-P	/	26	13.0
3	Cu NPs@MP-3	5.66	74	37.0
4	Cu NPs@SBA-15	5.43	55	27.5
5	Cu NPs@MP-1	2.95	63	31.5
6	Cu NPs@MP-2	4.37	69	34.5
7	Cu NPs@MP-4	6.87	64	32.0
8 ^c	Cu NPs@MP-3	5.66	96	48.0
9	Cu NPs@TMS-SBA-15	5.64	87	43.5

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Table 2 Catalytic performances of different Cu NPs-containing catalysts^{10,10,10,39/C7GC00219J}

^a Reaction conditions: phenylacetylene (0.50 mmol), benzoyl chloride (0.75 mmol), 1.0 mol% catalyst, Et₃N (1.5 mmol), 40°C, 6.0 h, N₂ atmosphere. ^b no catalyst ^c reaction time = 8.0 h ^d TON = n_{prod}/n_{cat} , which is defined as the total moles of product formed (n_{prod} .) divided by total moles of catalyst employed in the reaction (n_{cat} .).

Ynones are a class of alkynyl carbonyl compounds of considerable interest because they are important structural motifs in natural products. Meanwhile, they are usually employed as the precursors to prepare various valuable heterocyclic derivatives such as pyrroles, furans, furanones, pyrazoles, isoxazoles, indolizidinones, pyrimidines and pyridinones.³⁰ Recently, the catalytic coupling of acyl chlorides and terminal alkynes to ynones by using copper catalysts, known as the Sonogashira-type reaction, attracted much attention since this process avoids the use of a large amount of sensitive metal acetylides.³¹ To

View Article Online investigate the utility of our novel Cu NPs@MP catalysts, we firstly focused on the preparation of 1,3-diphenyl-2-propyn-1-one from benzoyl chloride and phenylacetylene. As shown in Table 2, the control test revealed that the blank experiment without the Cu-based catalyst didn't give any products (entry 1). Next, a series of Cu NPs@MP catalysts with different loadings were screened and the results showed that Cu NPs@MP-3 displayed the good conversion (74%) and excellent selectivity (100%) after 6.0 h. The inferior catalytic performances of Cu NPs@MP-1 and Cu NPs@MP-2 were probably attributed to the lower Cu NPs contents, which resulted in the decreased interaction between the reactants and the active sites. Meanwhile, the reduced catalytic efficiency of Cu NPs@MP-4 was maybe assigned to the smallest surface area and pore size, which increased the mass transfer resistance. Moreover, the bigger particle size and the broader particle dispersion decreased the accessibility of active species. Furthermore, the effect of the reaction parameters including catalyst amounts, reaction temperature and reaction time, different bases and solvents in the Cu NPs@MP-3 catalyzed model reaction was investigated (Table S1-S4). Satisfactorily, Cu NPs@MP-3 achieved the excellent conversion (96%) and selectivity (100%) by using triethylamine as the base at 40°C for 8.0 h under solvent-free condition.

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Figure 7 Water and toluene absorption tests of Cu NPs@MP-3 sample.

To explain this excellent catalytic performance of Cu NPs@MP-3, three control catalysts including the commercial Cu powder (Cu-P), mesoporous silica **SBA-15** supported nanoparticle NPs(a)SBA-15)Cu (Cu and trimethylsilyl-functionalized mesoporous silica **SBA-15** supported Cu nanoparticle (Cu NPs@TMS-SBA-15) were studied. In the same reaction conditions, the yields of Cu-P and Cu NPs@SBA-15 were 26% and 55%, respectively (Table 2). TEM image of Cu-P revealed that the Cu particles size was about 1-2 μ m (Figure S1). It represented the decreased surface active sites in comparison with Cu NPs@MP-3, resulting in the remarkable decrease in the activity. Furthermore, ICP tests (Table 1) confirmed the similar Cu loadings between Cu NPs@MP-3 and Cu NPs@SBA-15. Also, XRD pattern (Figure S2)

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and TEM picture (Figure S3) of Cu NPs@SBA-15 showed that it had the two-dimensional hexagonal ordered mesoporous structure and meanwhile Cu NPs with a size around 4.0 nm were highly dispersed in the mesoporous channels. Also, based on the N₂ sorption isotherm (Figure S4) of Cu NPs@SBA-15, the surface area, pore volume and pore size were determined as 565 m²/g, 5.2 nm and 0.60 cm³/g, respectively. Owing to their similar pore structures, we supposed the pore surface hydrophobicity played an important in their different reactivity. In order to prove this hypothesis, water and toluene vapor adsorption tests of Cu NPs@MP-3 were investigated. As shown in Figure 7, it exhibited the higher adsorption capacity (24.8%) for toluene and the lower adsorption capacity (10.9%) for water. These results clearly confirmed the pore surface of Cu NPs@MP-3 was hydrophobic, which can effectively stabilize and concentrate the reactants, especially for solvent-free reaction condition.³² To further confirm this phenomenon, Cu NPs@TMS-SBA-15 with hydrophobic groups was also prepared by using post-grafting approach. In comparison with Cu NPs@SBA-15, FT-IR spectrum (Figure S5) of Cu NPs@TMS-SBA-15 showed that the remarkable decrease intensity of the broad band around 3420 cm-1 indicative of Si-OH groups and the new vibration peaks around 2964 and 2906 cm-1 assigned to the stretching vibration of methyl groups clearly indicated the successful modification of TMS groups on the SBA-15 support. Accordingly, we tested the catalytic performance of Cu NPs@TMS-SBA-15 in the solvent-free Sonogashira reaction between phenylacetylene and benzoyl chloride.

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As expected, the yield was increased to 87%, which result further demonstrated the merit of hydrophobic pore surface. However, the inferior catalytic efficiency of Cu NPs@TMS-SBA-15 compared to Cu NPs@MP-3 was maybe due to the decreased surface area and pore size since the post-grafting treatment usually partially blocked the pore mouth or the pore channel.^{21b}

Entry	Acyl chlorides	Alkynes	Product	Yield (%)	TON ^b
1	CI			99	49.5
2	Cl	Br		85 Br	42.5
3	O CI	d.		96	48.0
4	O CI	0 ₂ N		71	35.5
5			+ ¹	99	49.5
6				83	41.5
7	Cl			71	35.5

Table 3 Reaction scope of Cu NPs@MP-3 catalyzed Sonogashira reactions^a

^a Reaction conditions: alkyne (0.5 mmol), acyl chloride (0.75 mmol), Et₃N (1.5 mmol), 1.0 mol% Cu NPs@MP-3, 40 °C, 8.0 h. ^bTON is defined as the total moles of product formed (n_{prod}) divided by total moles of catalyst employed in the reaction (n_{cat}). TON = n_{prod}/n_{cat} .

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Encouraged by the above results, we extended the scope of this solvent-free Sonogashira reaction by using various derivatives of acyl chlorides and terminal alkynes. As shown in Table 3, the reaction with various derivatives of phenylacetylene with substituents such as methyl, bromo, chloro, and nitro also gave good yields of the corresponding products (entry 1-4). Also, aliphatic chloride reacted smoothly with terminal alkyne (entry 5). Furthermore, benzoyl chloride substituted with methoxy group still gave the the corresponding ynones in excellent yield (entry 6). Under the same conditions, cyclic alkyne derivatives afforded the desired product with the moderate yield (entry 7).

An important advantage of Cu NPs@MP-3 catalyst was its easy recycle and reuse.³³ Figure 8 showed the recyclability of the Cu NPs@MP-3 catalyst during solvent-free Sonogashira reaction between benzoyl chloride and phenylacetylene. No significant reduce was found in the yields after being used repetitively ten times, which exceeded the best results previously reported in the literature. ICP analysis revealed that the copper content was 5.65 wt.% in the recycled Cu NPs@MP-3 catalyst, which indicated that only about 0.17% of the Cu species leached off after ten cycles. This result confirmed that the mesoporous structure could inhibit the Cu NPs leaching. Moreover, low-angle XRD pattern (Figure S6) demonstrated that ordered 2-D mesostructure was preserved after the recycle test. N₂ sorption isotherm showed the typical type IV isotherm with the capillary condensation step (Figure S7). However, the surface area and pore size were 206 m^2/g and 3.1 nm, respectively (Table 1). Also, TEM image (Figure S8) revealed

that the partial particle aggregation existed, which probably caused the decrease of catalytic activity of Cu NPs@MP-3 after ten repetitions. Thus, these results was maybe responsible for the slight decrease reactivity of the recycled Cu NPs@MP-3 catalyst after ten repetitions.³⁴



Figure 8 Recycling tests of Cu NPs@MP-3 catalyst in solvent-free Sonogashira reaction between benzoyl chloride and phenylacetylene. Reaction conditions were in Table 3.

Conclusion

In summary, we have developed a facile approach to prepare highly active mesoporous polymer supported copper nanoparticles (Cu NPs@MP) through the incorporation of copper nitrate hydrates into the support by melt infiltration and

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the subsequent in-situ reduction of Cu(II) ions by template pyrolysis. Notably, it displayed the remarkable increase in the catalytic activity in solvent-free Sonogashira reactions between acyl chlorides and terminal alkynes compared to the commercial Cu powder. In comparison with mesoporous silica SBA-15 supported Cu nanoparticles, it also exhibited the higher catalytic reactivity. The analysis demonstrated that systematic the mesoporous structure, the monodispersed Cu nanoparticles and the surface hydrophobicity could enrich the reactants and increase the accessibility of active sites as well as reduce the diffusion limitation. Moreover, it could be easily recycled reused at least ten times without the significant loss of catalytic activity. This work provides a general approach towards the facile and green preparation of a large variety of supported base metals nanoparticles for more environmental friendly chemical transformations.

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Notes and references

[1] (a) S. E. Allen, R. R. Walvoord, R. Padilla-Salinas, M. C. Kozlowski, Chem.

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Rev. 2013, **113**, 6234-6458; (b) B. Su, Z. C. Cao. Z. J. Shi, *Acc. Chem. Res.* 2013, **48**, 886-896.

- [2] B. C. Ranu, R. Dey, T. Chatterjee, S. Ahammed, *ChemSusChem* 2012, 5, 22-44.
- [3] (a) R. B. N. Baig, R. S. Varma, *Green Chem.* 2012, 14, 625-632; (b) R.
 Hudson, C. J. Li, A. Moores, *Green Chem.* 2012, 14, 622-624.
- [4] (a) A. Fedorov, H. Liu, H. Lo, C. Copéret, J. Am. Chem. Soc. 2016, 138,
- 16502-16507; (b) W. Gao. Y. F. Zhao, H. R. Chen, H. Chen, Y. W. Li, S. He, Y. K.
- Zhang, M. Wei, D. G. Evans, X. Duan, Green Chem. 2015, 17, 1525-1534.

Published on 24 March 2017. Downloaded by University of Newcastle on 24/03/2017 16:48:46.

- [5] (a) B. Rungtaweevoranit, J. Baek, J. R. Araujo, B. S. Archanjo, K. M. Choi,
- O. M. Yaghi, G. A. Somorjai, *Nano Lett.* 2016, 16, 7645-7649; (b) K. S. Gayen, T. Sengupta, Y. Saima, A. Das, D. K. Maiti, A. Mitra, *Green Chem.* 2012, 14, 1589-1592.
- [6] F. Wang, R. Shi, Z. Q. Liu, P. J. Shang, X. Pang, S. Shen, Z. Feng, C. Li, W. Shen, ACS Catal. 2013, 3, 890-894.
- [7] B. J. Borah, D. Dutta, P. P. Saikia, N. C. Barua, D. K. Dutta, *Green Chem.*2011, 13, 3453-3460.
- [8] M. B. Gawande, A. Goswami, F. Felpin, T. Asefa, X. X. Huang, R. Silva, X.
 X. Zou, R. Zboril, R. S. Varma, *Chem. Rev.* 2016, **116**, 3722-3811.
- [9] D. Mott, J. Galkowski, L. Y. Wang, J. Luo, C. J. Zhong, *Langmuir* 2007, 23, 5740-5745.
- [10] J. F. Blandez, A. Primo, A. M. Asiri, M. M. Alvaro, H. García, Angew.

Green Chemistry

Chem. Int. Ed. 2014, 53, 12581-12586.

- [11] K. Larmier, S. Tada, A. Comas-Vives, C. Copéret, J. Phys. Chem. Lett. 2016, 7, 3259-3263.
- [12] D. Wang, G. H. Yang, Q. X. Ma, M. B. Wu. Y. S. Tan, Y. Yoneyama, N. Tsubaki, ACS Catal. 2012, 2, 1958-1966.
- [13] Y. F. Wang, A. V. Biradar, G. Wang, K. K. Sharma, C. T. Duncan, S. Rangan,T. Asefa, *Chem. Eur. J.* 2010, 16, 10735-10743.
- [14] Y. Yin, W. J. Jiang, X. Q. Liu, Y. H. Li, L. B. Sun, J. Mater. Chem. 2012, 22, 18514-18521.
- [15] (a) T. M. Eggenhuisen, J. P. den Breejen, D. Verdoes, P. E. de Jongh, K. P. de Jong, J. Am. Chem. Soc. 2010, 132, 18318-18325; (b) P. E. de Jongh, T. M. Eggenhuisen, Adv. Mater. 2013, 25, 6672-6690.
- [16] Y. Wang, Z. Wu, L. Shi, J. Zhu, Adv. Mater. 2005, 17, 323-327.
- [17] P. Munnik, P. E. de Jongh, K. P. de Jong, J. Am. Chem. Soc. 2014, 136, 7333-7340.
- [18] W. J. Jiang, Y. Yin, X. Q. Liu, X. Q. Yin, Y. Q. Shi, L. B. Sun, J. Am. Chem. Soc. 2013, 135, 8137-8140.
- [19] F. Zhang, Y. Meng, D. Gu, Y. Yan, C. Yu, B. Tu and D. Zhao, J. Am. Chem. Soc. 2005, 127, 13508-13509.
- [20] (a) R. Xing, Y. M. Liu, H. H. Wu, X. H. Li, M. Y. He, P. Wu, *Chem. Commun.* 2008, 44, 6297-6299; (b) J. Mondal, S. K. Kundu, W. K. H. Ng, R. Singuru, P. Borah, H. Hirao, Y. L. Zhao, A. Bhaumik, *Chem. Eur. J.* 2015, 21,

Green Chemistry Accepted Manuscrip

View Article Online

19016-19027; (c) J. Mondal, A. Biswas, S. Chiba, Y. L. Zhao, *Sci*.¹⁰*Rep*. 2015, **8**, 98294.

[21] (a) D. Y. Zhao, Q. S. Huo, J. L. Feng, B. F. Chmelka, G. D. Stucky, J. Am. *Chem. Soc.* 1998, **120**, 6024-6036. (b) T. X. Bui, S. Y. Kang, S. H. Lee, H. Choi,
J. Hazard. Mater. 2011, **193**, 156-163.

- [22] Y. F. Zhu, X. Kong, X. Q. Li, G. Q. Ding, Y. L. Zhu, Y. W. Li, ACS Catal.2014, 4, 3612-3620.
- [23] A. N. Pestryakov, V. P. Petranovskii, A. Kryazhov, O. Ozhereliev, N.Pfänder, A. Knop-Gericke, *Chem. Phys. Lett.* 2004, **385**, 173-176.

[24] (a) F. Bérubé, S. Kaliaguine, *Microporous Mesoporous Mater.* 2008, 115, 469-479. (b) F. D. Kopinke, M. Remmler, K. Mackenzie, M. Möder, O. Wachsen, *Polym. Degrad. Stab.* 1996, 53, 329-342.

[25] C. S. Chen, C. C. Chen, C. T. Chen, H. M. Kao, *Chem. Commun.* 2011, 47, 2288-2290.

[26] F. Zhang, C. Liang, M. Z. Chen, H. B. Guo, H. Y. Jiang, H. X. Li, Green Chem. 2013, 15, 2865-2871.

[27] L. Li, J. L. Shi, L. M. Xiong, L. X. Zhang, J. N. Yan, Adv. Mater. 2004, 16, 1079-1082.

[28] F. Zhang, J. W. Yin, W. Chai, H. X. Li, ChemSusChem 2010, 3, 724-727.

[29] S. Megarajan, K. B. A. Ahmed, R. Rajmohan, P. Vairaprakash, V. Anbazhagan, RSC Adv. 2016, 6, 103065-103071.

[30] (a) D. A. Alonso, C. Nájera, M. C. Pacheco, J. Org. Chem. 2004, 69,

- View Article Online 1615-1619; (b) Z. F. Wang, L. Li, Y. Huang, J. Am. Chem. Soc. 2014, **136**, 12233-12236.
- [31] (a) W. J. Sun, Y. Wang, X. Wu, X. Q. Yao, Green Chem. 2013, 15,
- 2356-2360; (b) M. A. Bhosale, T. Sasaki, B. M. Bhanage, Catal. Sci. Technol. 2014, 4, 4274-4280.
- [32] F. Zhang, H. X. Li, Chem. Sci. 2014, 5, 3695-3707.
- [33] S. Wang, Q. F. Zhao, H. M. Wei, J. Q. Wang, M. Cho, H. S. Cho, O. Terasaki, Y. Wan, J. Am. Chem. Soc. 2013, 135, 11849-11860.
- [34] S. Ikurumi, S. Okada, K. Nakatsuka, T. Kamegawa, K. Mori, H. Yamashita,
- J. Phy. Chem. C 2014, 114, 575-581.

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A facile synthesis of copper nanoparticles supported on ordered mesoporous polymer was developed for solvent-free Sonogashira coupling reactions.