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Article

On the comparable activity in plasmonic photocatalytic and thermocatalytic oxidative homocoupling of alkynes over prereduced copper ferrite

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ABSTRACT

Despite of extensive attention on the copper-based heterogeneous oxidative homocoupling of alkynes (OHA) to 1,3-diynes, the photocatalytic OHA is scarcely investigated. By screening copper-containing spinel catalysts, we discovered that a prereduced copper ferrite (CuFe_2O_4) not only can catalyze the thermocatalytic OHA but also is efficient for the photocatalytic OHA under visible light irradiation. It is found that the sol-gel combustion (SG) method and the partial reduction at 250 °C can result in the optimal CuFe_2O_4 -SG-250 catalyst showing high activity and stability. Surface oxidized Cu_2O is evidenced to be the active species for the thermocatalytic OHA, whereas metallic copper nanoparticles (CuNPs) are identified as the active sites for the photocatalytic OHA. The efficiency of photocatalytic OHA at ambient temperature is comparable to that of thermocatalytic OHA at 120 °C, and the CuFe_2O_4 -SG-250 catalyst can be magnetically separated and reused at least five times. The localized surface plasmon resonance effect of CuNPs contributes to visible light-induced photocatalytic OHA.

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1. Introduction

Considerable attention has been paid to the development of efficient methods for the synthesis of conjugated 1,3-diynes, because these compounds are important building blocks for the synthesis of natural products, pharmaceuticals, optoelectronic materials and polymers [1–3]. Copper-catalyzed oxidative homocoupling of alkynes (OHA), also known as Glaser-Hay coupling, is considered a classic route to the symmetrical conjugated 1,3-diynes [4–6]. From a practical viewpoint, heterogeneous copper catalysts are more advantageous over the homogeneous counterparts due to their easy recovery and recycling as well as enhanced stability [6–8]. Although various support

materials have been used to immobilize copper species for the OHA reactions, most of the heterogeneous systems are effective only in the presence of nitrogen-containing ligands or base additives [7,9–19], which usually bring corrosion and pollution problem. Therefore, it is an attractive and challenging goal to develop efficient heterogeneous copper catalysts that can perform the green synthesis of conjugated 1,3-diynes under ligand- and base-free conditions.

To address the above challenge, inorganic oxide-supported copper catalysts have been explored [20–26]. Mixed oxides containing undefined $\text{Cu}^+/\text{Cu}^{2+}$ composition, such as $\text{Cu}(\text{OH})_x/\text{MnO}_2$ [22], $\text{CuO}_x/\text{TiO}_2$ [23,24], $\text{CuO}_x/\text{MnO}_x$ [25] and $\text{CuO}_x/\text{Fe}_3\text{O}_4$ [26] were used as recyclable catalysts for the addi-

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tive-free OHA in toluene at 90–180 °C. Despite these important progress, the nature of active copper species remains unclear. For practical application, if the heterogeneous additive-free OHA reaction can be readily carried out at room temperature (RT), it would remarkably reduce energy consumption and be more economically competitive and environmentally benign. However, examples of such green OHA process are scarce.

The utilization of solar energy to drive catalytic chemical transformations is one of the most promising strategies to substantially reduce the energy consumption in the future [27]. Especially, visible light-induced transition metal-catalyzed organic reactions are recognized as powerful alternatives to metal-catalyzed “thermal” reactions, since visible light-mediated reactions are normally performed at RT in the absence of ligands or bases [28]. Visible light-induced copper-catalyzed homogeneous reactions in the absence of exogenous photosensitizers mainly involve C–C and C–N coupling, and C≡C oxidation reactions [29]. Hwang’s group firstly reported a visible light-induced OHA reaction at RT with CuCl as the catalyst in CH₃CN under blue LED irradiation [30]. For heterogeneous photocatalytic organic reactions over copper catalysts, there are only few reports focused on the localized surface plasmon resonance (LSPR) effect of copper nanoparticles (CuNPs) for alkene epoxidation, C–N/C–O/C–S and N–N couplings [31–36]. To our knowledge, visible light-driven heterogeneous copper-catalyzed OHA reaction has not yet been reported.

Since Cu⁺ species plays important role in homogeneous photocatalytic and heterogeneous thermocatalytic OHA reactions, there would be opportunity to use Cu⁺-containing mixed oxides to develop effective heterogeneous photocatalyst for additive-free OHA reactions. Intrigued by our previous findings on the synergistic effect of Cu⁺-containing spinel supports on the oxidative dehydrogenation of alcohol [37–41], we employed these Cu⁺-containing chromite, aluminate and ferrite spinels in exploring the heterogeneous thermocatalytic and photocatalytic OHA reactions under additive-free conditions. The results evidently indicate that catalyst pretreatment by H₂ is crucial for both the thermocatalytic and photocatalytic reactions, and copper ferrite (CuFe₂O₄) outperforms the other spinels. Surprisingly, the photocatalytic OHA under visible light irradiation at RT shows comparable catalytic efficiency to the thermocatalytic OHA at 120 °C. Furthermore, the preparation method of CuFe₂O₄ and the pretreatment temperature strongly influence the catalytic performance. Controlled experiments demonstrate that surface oxidized Cu₂O is the active species for the thermocatalytic OHA and metallic CuNPs are the active species for the photocatalysis. The LSPR effect of CuNPs contributes to the visible light-induced photocatalytic OHA.

2. Experimental

2.1. Materials

Metal nitrates (Cu(NO₃)₂·3H₂O, Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Cr(NO₃)₃·9H₂O, Fe(NO₃)₃·9H₂O), citric acid, ethylene glycol, and various analytically pure solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. Copper

(I) oxide (Cu₂O, 99%), cupric oxide (CuO, 99%), phenylacetylene (97%), 4-methoxy-phenylacetylene (98%), 4-methyl-phenylacetylene (98%), 4-Cl-phenylacetylene (98%), 1,4-diphenylbutadiyne (98%) and *n*-dodecane (99%) were purchased from Adamas Reagent Co., Ltd. 1-heptyne (99%), propargyl acetate (97%) and copper powder (Cu⁰, 99.9%) were purchased from Alfa Aesar. 3-methyl-phenylacetylene (98%) was purchased from TCI. Triiron tetraoxide (Fe₃O₄, 97%) and titanium dioxide (TiO₂, 99.5%) were purchased from Aldrich. All chemicals were used as received.

2.2. Catalyst preparation

Spinel (MgCuCr₂O₄, CuCr₂O₄, MgCuAl₂O₄, CuAl₂O₄, MgCuFe₂O₄, CuFe₂O₄) prepared by co-precipitation method (designated as spinel-CP hereafter), in which the ternary MgCuM₂O₄ (M = Cr, Al, Fe) is the abbreviation of Mg_{0.75}Cu_{0.25}M₂O₄, were reported in our previous paper [41] and used directly in this work. To prepare CuFe₂O₄ by a different method, a sol-gel combustion (SG) method was employed as follows: the nitrates containing Cu²⁺ and Fe³⁺ in the stoichiometric quantity for synthesis of 10 g of the product were dissolved in deionized water (50 mL), then citric acid (6 g) and ethylene glycol (3 mL) were added; the resulting solution was evaporated in a sand bath, in the end, the gel mixture got inflamed to produce an amorphous precursor; the precursor was calcined in air at 700 °C for 5 h to yield the CuFe₂O₄-SG sample. The CuFe₂O₄-SG was pretreated by H₂ at 150, 200, 250 and 300 °C to give CuFe₂O₄-SG-150, CuFe₂O₄-SG-200, CuFe₂O₄-SG-250 and CuFe₂O₄-SG-300 catalysts, respectively. Similarly, the spinel-CP samples were pretreated by H₂ to afford spinel-CP-T catalysts, where T is the reduction temperature. The reference Cu/Fe₃O₄ and Cu/TiO₂ catalysts with 5 wt% copper loading were prepared by incipient wetness impregnation using Cu(NO₃)₂·3H₂O aqueous solution. After impregnation, the paste precursors were dried at 60 °C for 12 h, then the catalysts were obtained by treating with 10 vol% H₂ at 350 °C for 2 h.

2.3. Catalyst characterization

X-ray diffraction (XRD) was performed on an Empyrean apparatus using Cu K_α radiation (40 kV and 30 mA). Nitrogen physisorption was done on a Tristar 3000 automated gas adsorption system. High resolution transmission electron microscopy (HRTEM) images were acquired on a FEI Tecnai G2 F30 electron microscope. The magnetization and coercivity of the CuFe₂O₄ samples were measured by using a Model 3472-70 GMW vibrating sample magnetometer (VSM) with a maximum magnetic field of 15 kOe. The amount of surface acid-dissolvable copper species was determined by a Perkin Elmer AA-300 atomic absorption spectrometer (AAS) after treating the mixed oxides in nitric acid. Ultraviolet-visible (UV-vis) spectra were recorded by a Varian Cary 5000 spectrophotometer in a diffusion reflectance mode with BaSO₄ as a reference. Temperature-programmed reduction (TPR) experiments were performed on Micrometrics AutoChem 2920II instrument. Typically, 20 mg of the sample was loaded in a

U-shape quartz tube and pretreated in Ar at 350 °C for 1 h. After cooling to room temperature in flowing Ar, the sample was reduced in 10 vol% H₂ in Ar at a flow rate of 10 mL/min, while it was heated from room temperature up to 800 °C at a ramp rate of 10 °C/min. The outlet gas was detected by the thermal conductivity detector. X-ray photoelectron spectroscopic (XPS) measurements were conducted on an AXIS-ULTRA DLD-600W spectrometer with Al K α irradiation and the binding energies were calibrated by using the C 1s peak of contaminant carbon at 284.5 eV as an internal standard.

2.4. Catalytic tests

For thermocatalytic OHA reactions, a typical procedure is as follows. A mixture of alkyne (0.2 mmol), *n*-dodecane (0.1 mmol, as internal standard), spinel or reduced spinel catalysts (20 mg), and dimethylsulfoxide (DMSO, 2 mL) was added into a 15 mL Pyrex glass tube (ϕ 15 mm) equipped with a condenser and an oxygen balloon. The reaction mixture was heated to 120 °C under vigorous stirring (700 rpm) for the required time. After the reaction was stopped by addition of ethyl acetate (5 mL), a portion of the mixture (1 mL) was filtered through a Titan filter (pore size 0.22 μ m) to remove the catalyst particulates. The products were qualitatively analyzed by an Agilent 7890A/5975C GC-MS. Quantitative analysis was done on a Fuli 9070 GC-FID using an internal standard technique. In all cases, 1,3-diyne was the only product with 100% selectivity and the carbon balances were 100% $\pm$ 3%.

Photocatalytic OHA reactions were conducted in a light-reaction chamber connected to an air conditioner, which keeps room temperature at 20 °C. Typically, a mixture of alkyne (0.2 mmol), *n*-dodecane (0.1 mmol, as internal standard), reduced spinel catalysts (20 mg), and ethanol (2 mL) was added into a 15 mL Pyrex glass tube (ϕ 15 mm) equipped with an oxygen balloon and a temperature meter. Then the tube was

stirred magnetically (700 rpm) at RT and irradiated with visible light of a light-emitting diode (PLS-LED 100, Beijing Perfect-light Technology Co. LTD). Four LED light sources with different wavelength in the range of 400–500/480–580/580–680/400–780 nm were used and denoted as blue/green/red/white LED hereafter, respectively. The light intensity was set to 0.2 W/cm² unless otherwise specified. Due to the heating effect of LED irradiation, the reaction in the dark was maintained the same temperature (30 °C) as the photocatalytic reaction to make sure that the comparison is meaningful. All the reactions in the dark were conducted using a water bath and the tube was wrapped with aluminum foil. After the reaction, similar treatment and analysis procedures as the above thermocatalytic reaction were performed. In all cases, 1,3-diyne was the only product with 100% selectivity and the carbon balances were 100% $\pm$ 3%.

3. Results and discussion

3.1. Screening catalysts for thermocatalytic and photocatalytic OHA

We initially studied the thermocatalytic oxidative homocoupling of phenylacetylene over the untreated spinel-CP samples under the similar reaction conditions (at 110 °C for 3 h in toluene) as the CuO_x/TiO₂-catalyzed OHA reactions [24]. However, various spinels showed negligible activity (1,3-diyne yield < 1%). The very low activity of the spinel-CP samples may be due to their low surface area (4–14 m²/g) and thus low surface available copper species. To increase the surface copper species, all spinel-CP samples were pretreated by 10% H₂ in N₂ at 300 °C for 2 h. Because CuFe₂O₄-CP is the most reducible and could be reduced to Cu⁰ and Fe₃O₄ below 300 °C [41], we employed the CuFe₂O₄-CP-300 to screen the reaction solvent and temperature (Table 1). To our delight, the OHA reaction per-

Table 1

Thermocatalytic and photocatalytic oxidative homocoupling of phenylacetylene over various catalysts.

Entry	Catalyst	Thermocatalytic OHA ^a			Photocatalytic OHA ^b		
		Solvent	Temp. (°C)	Yield ^c (%)	Solvent	Temp. (°C)	Yield ^c (%)
1	CuFe ₂ O ₄ -CP-300	EtOH	80	<1	DMSO	30	66
2	CuFe ₂ O ₄ -CP-300	CH ₃ CN	80	2	DMF	30	43
3	CuFe ₂ O ₄ -CP-300	Dioxane	100	<1	Toluene	30	3
4	CuFe ₂ O ₄ -CP-300	Toluene	110	<1	Dioxane	30	6
5	CuFe ₂ O ₄ -CP-300	DMF	120	10	THF	30	7
6	CuFe ₂ O ₄ -CP-300	DMSO	90	13	CH ₃ CN	30	76
7	CuFe ₂ O ₄ -CP-300	DMSO	100	20	i-PrOH	30	70
8	CuFe ₂ O ₄ -CP-300	DMSO	110	50	MeOH	30	89
9	CuFe ₂ O ₄ -CP-300	DMSO	120	88	EtOH	30	92
10	MgCuFe ₂ O ₄ -CP-300	DMSO	120	5	EtOH	30	17
11	CuCr ₂ O ₄ -CP-300	DMSO	120	75	EtOH	30	53
12	MgCuCr ₂ O ₄ -CP-300	DMSO	120	49	EtOH	30	1
13	CuAl ₂ O ₄ -CP-300	DMSO	120	50	EtOH	30	34
14	MgCuAl ₂ O ₄ -CP-300	DMSO	120	3	EtOH	30	24

Reaction conditions: phenylacetylene (0.2 mmol), *n*-dodecane (0.1 mmol) and catalyst (20 mg) in the solvent (2 mL) under an O₂ atmosphere for 3 h. ^a Thermocatalytic OHA reaction was carried out by heating at certain temperature. ^b Photocatalytic OHA reaction was performed under white LED irradiation (0.2 W/cm²) at ambient temperature (30 °C). ^c Yields were determined by GC.

formed in DMSO at 120 °C for 3 h can achieve the highest 1,3-diyne yield (88%), which is comparable to the best results obtained by the previously reported preferred $\text{CuO}_x/\text{TiO}_2$ (yield up to 94%) [24]. Under the identical reaction conditions, the other spinel-CP-300 catalysts showed inferior activity to the CuFe_2O_4 -CP-300, primarily due to the lower surface copper species in the former. It is needed to point out that the unreduced spinel-CP samples showed no activity even under the optimal conditions.

With the aim to develop green heterogeneous photocatalytic OHA reaction at RT, we employed white LED as light source because of its lower cost and energy consumption than a halogen lamp. Firstly, we investigated the effect of various solvents on the CuFe_2O_4 -CP-300-catalyzed oxidative homocoupling of phenylacetylene under visible light irradiation (Table 1). Polar solvents are better than nonpolar solvents in this heterogeneous photocatalytic OHA reaction. Some polar solvents, such as DMSO, CH_3CN , 2-PrOH and MeOH, resulted in moderate to high yield (66%–89%) of 1,3-diyne. Interestingly, when the nontoxic EtOH was used as a solvent, the highest yield (92%) was achieved. With ethanol as the optimal solvent, the other spinel-CP-300 catalysts also showed much lower activity than the CuFe_2O_4 -CP-300. In contrast, the unreduced spinel-CP samples are inactive in the photocatalytic OHA and the CuFe_2O_4 -CP-300 shows no activity in the dark even at 80 °C (Table 1, entry 1). Undoubtedly, we found a novel CuFe_2O_4 -CP-300 photocatalyst, which is efficient for the heterogeneous photocatalytic OHA under visible light irradiation.

On the basis of above results, it is evident that the reducibility and the amount of surface copper species of the CuFe_2O_4 spinel is crucial for both the thermocatalytic and the photocatalytic OHA reactions. Since the reducibility and surface composition of mixed oxides can be tuned by different preparation methods and reduction temperatures [40–43], there would be great opportunity to further enhance the catalytic efficiency by improving the reducibility and surface copper species of copper ferrite.

3.2. Optimization of the prereduced CuFe_2O_4 catalyst

Among various preparation methods for CuFe_2O_4 spinel, such as co-precipitation (CP), sol-gel combustion (SG), hydrothermal, microwave and solid-state reaction [41–44], the CP and SG methods are more attractive and advantageous due to the simpler operation, higher product purity and crystallinity. Compared to the CP method, the citrate-assisted SG method can save the tedious filtration and washing steps. Therefore, besides the CuFe_2O_4 -CP sample, we also employed the SG method to prepare the CuFe_2O_4 -SG sample, which showed even lower surface area (3 m^2/g) than the CuFe_2O_4 -CP (5 m^2/g). Furthermore, the CuFe_2O_4 -CP and CuFe_2O_4 -SG samples were pretreated in H_2 at different temperatures to provide a series of reduced CuFe_2O_4 samples with different amount of surface copper species.

Fig. 1 shows the XRD patterns of various reduced CuFe_2O_4 samples. With the reduction temperature increasing from 150 to 300 °C, the CuFe_2O_4 -spinel phase (JCPDS 34-0425) gradually

Fig. 1. XRD patterns of various reduced CuFe_2O_4 -CP and CuFe_2O_4 -SG samples.

changed to the mixture of Fe_3O_4 phase (JCPDS 19-0629) and metallic Cu^0 phase (JCPDS 04-0836). Interestingly, the CuFe_2O_4 -SG sample showed higher reducibility than the CuFe_2O_4 -CP, with Fe_3O_4 phase appearing at 200 °C in the former but at 250 °C in the latter. These XRD results are consistent with the H_2 -TPR results (Fig. 2), which confirm that the reduction of CuFe_2O_4 -spinel to Cu^0 and Fe_3O_4 starts below 200 °C for the CuFe_2O_4 -SG and above 200 °C for the CuFe_2O_4 -CP. The AAS results evidently indicated that the acid-dissolvable copper species of the reduced CuFe_2O_4 -SG (mainly Cu^0 and its air-oxidized products such as Cu_2O and CuO) increased from 2.5 to 22.5 wt% with the reduction temperature increasing from 150 to 300 °C. For the CuFe_2O_4 -SG-200, CuFe_2O_4 -SG-250, CuFe_2O_4 -CP-250 and CuFe_2O_4 -CP-300 samples, the fractions of the acid-dissolvable copper species were 7.7, 16.8, 4.3 and 20.7 wt%, respectively, which are lower than the theoretical value (26.6 wt%) for the completely reduced CuFe_2O_4 . It is noteworthy

Fig. 2. TPR profiles showing H_2 consumption for CuFe_2O_4 -CP and CuFe_2O_4 -SG samples.

thy that no acid-dissolvable copper species was detected for the unreduced CuFe_2O_4 -CP and CuFe_2O_4 -SG samples. The HRTEM images of the reduced CuFe_2O_4 -CP-300 and CuFe_2O_4 -SG-250 (Fig. 3) also indicated the presence of metallic Cu^0 and Fe_3O_4 phases. Lattice fringes of (111) planes for Cu^0 and (311) planes for Fe_3O_4 were clearly observed, with the d spacing distance around 0.21 and 0.25 nm, respectively. These d spacing data are in agreement with the XRD results.

The magnetic properties of the unreduced and reduced CuFe_2O_4 samples were examined by a vibrating sample magnetometer at room temperature (Fig. S1). The obtained magnetization hysteresis loops show a typical ferromagnetic behavior with a S-shape [43]. For the CuFe_2O_4 -SG-250 and CuFe_2O_4 -CP-300 samples, their magnetization hysteresis loops are similar to the previously reported Fe_3O_4 nanoparticles [45,46], illustrating that these samples are superparamagnetic. Moreover, all the reduced CuFe_2O_4 samples can be facily separated with a magnet, which is beneficial to catalyst recycling.

The light absorptions of the unreduced and reduced CuFe_2O_4 samples were examined by diffuse reflectance UV-vis spectra (Fig. 4). The unreduced CuFe_2O_4 -CP and CuFe_2O_4 -SG samples exhibit similar strong light absorption in the UV-vis region in the wavelength of 220–800 nm, with the maximum absorption at 600 nm. In contrast, there is an obvious improvement in light absorption for the reduced CuFe_2O_4 -CP-300 and CuFe_2O_4 -SG-250, especially in the range of visible light. A distinguishable absorption peak at around 570 nm was observed for both reduced samples, which can be attributed to the LSPR absorption of CuNPs [33,34]. The enhanced visible light absorption of the reduced CuFe_2O_4 samples is consistent with the color change from brown to black after H_2 reduction, and is conducive for the photocatalytic reaction irradiated by white LED.

We next studied the thermocatalytic and photocatalytic oxidative homocoupling of phenylacetylene over the various reduced CuFe_2O_4 -CP and CuFe_2O_4 -SG catalysts under the optimal reaction conditions as shown in Table 1 (Fig. 5). Interestingly, the reduced CuFe_2O_4 -SG catalysts showed much higher activity than the corresponding CuFe_2O_4 -CP catalysts in both thermocatalytic and photocatalytic OHA, primarily due to the more surface copper species in the former cases. Moreover, the catalytic activity increased with the reduction temperature in all cases. The CuFe_2O_4 -CP-300 showed a drastic increase in activity compared to the CuFe_2O_4 -CP-250, because the fraction of

Fig. 4. UV-vis absorption spectra of typical unreduced and reduced CuFe_2O_4 samples.

acid-dissolvable copper species in the former (20.7 wt%) is much higher than the latter (4.3 wt%). In contrast, the CuFe_2O_4 -SG-250 exhibited higher activity than the CuFe_2O_4 -CP-300, and the former catalyst achieved up to 90% and 95% yield of 1,3-diyne in the thermocatalytic and photocatalytic OHA, respectively. The similar catalytic activation in the thermocatalytic and photocatalytic reactions may be attributed to the similar amount of active copper species. It is evident that the activity of photocatalytic OHA at RT can be superior to that of thermocatalytic OHA at 120 °C. Compared to the CuFe_2O_4 -SG-300, the CuFe_2O_4 -SG-250 showed similar activity, suggesting that the moderate amount of surface copper species in the former is sufficient for the OHA reaction. Therefore, we selected the CuFe_2O_4 -SG-250 as the optimal catalyst for further studies.

Fig. 3. HRTEM images for CuFe_2O_4 -CP-300 (a) and CuFe_2O_4 -SG-250 (b) samples.

Fig. 5. Influence of preparation method and reduction temperature of CuFe_2O_4 on the catalytic activity in the thermocatalytic and photocatalytic oxidative homocoupling of phenylacetylene under the optimal reaction conditions listed in Table 1.

Fig. 6. Time course of 1,3-diyne yield in the thermocatalytic and photocatalytic oxidative homocoupling of phenylacetylene by using fresh and recycled CuFe_2O_4 -SG-250 catalysts.

3.3. Identification of active copper species in thermocatalytic and photocatalytic OHA

Since the unreduced CuFe_2O_4 -spinel and bare Fe_3O_4 show no catalytic activity in both thermocatalytic and photocatalytic OHA, copper is thought to be the active site. Although metallic CuNPs enrich in the surface of the fresh CuFe_2O_4 -SG-250, they

are prone to oxidation to form Cu_2O and CuO under the O_2 atmosphere during the OHA reactions. Therefore, it is of importance to clarify the active copper species in the thermocatalytic and photocatalytic OHA. We firstly established the time course of yield of 1,3-diyne to evaluate the influence of the oxidation state change of copper on the catalytic activity (Fig. 6). Evidently, an induction period was observed for the thermocatalytic OHA, indicating that the active copper species is not the metallic Cu^0 but the oxidized Cu^+ or Cu^{2+} . In line with this, the induction period was absent in the second reaction cycle, likely due to the presence of abundant surface Cu^+ or Cu^{2+} species in the recycled CuFe_2O_4 -SG-250 catalyst. For the photocatalytic OHA, in contrast, there was no induction period for the first reaction cycle, suggesting that metallic Cu^0 is an active site. However, a significant decrease in activity was observed for the second cycle, primarily due to the facile oxidation of surface CuNPs by O_2 during the reaction and the recycling. After the solid catalyst was removed at about 50% conversion of phenylacetylene, no further OHA was detected in the supernatant after 2 h under the same conditions. These results demonstrate that CuFe_2O_4 -SG-250 acts as a real heterogeneous catalyst in both thermocatalytic and photocatalytic OHA.

XPS was used to clarify the changes of surface copper, iron and oxygen species for the fresh CuFe_2O_4 -SG-250 catalyst and the one after reuse for the thermocatalytic and photocatalytic OHA reactions (Fig. 7). In the $\text{Cu } 2p_{3/2}$ XPS spectra, Cu^{2+} species

Fig. 7. XPS spectra of the fresh (a), thermocatalytically reused (b) and photocatalytically reused (c) CuFe_2O_4 -SG-250 catalysts. (A) Cu 2p; (B) Cu LMM; (C) Fe 2p; (D) O 1s.

appear at ~934 eV [37,47], accompanied by the Cu^{2+} shakeup satellite peaks (938–945 eV). The lower binding energy (BE) peak at ~932.2 eV in the fresh and reused CuFe_2O_4 -SG-250 catalyst suggests the presence of Cu^+ or Cu^0 species [40,48]. Because Cu $2p_{3/2}$ XPS cannot differentiate between Cu^+ and Cu^0 , Auger Cu LMM spectra were used to confirm the presence of Cu^0 , Cu^{2+} and Cu^+ species in the fresh CuFe_2O_4 -SG-250 catalyst with the BE peak at ~567.1, 568.5 and 569.8 eV [42,49], respectively. The relatively low Cu^0 fraction (10%) and high $\text{Cu}^+/\text{Cu}^{2+}$ fraction in the fresh catalyst can be due to the facile oxidation of CuNPs in air [32]. It is worth noting that the surface $\text{Cu}^0/\text{Cu}^+/\text{Cu}^{2+}$ fractions vary with the exposure time in air for the fresh catalyst, with longer exposure resulting in higher $\text{Cu}^+/\text{Cu}^{2+}$ fractions. The Cu LMM spectra in Fig. 7(B) suggested the absence of Cu^0 species in the reused catalysts, with the surface Cu^+ fractions being 28% and 65% for the thermocatalytically and photocatalytically reused catalysts, respectively. These results indicate that the high reaction temperature in the thermocatalytic OHA facilitates the oxidation of surface Cu^0 and Cu_2O species to CuO . In the Fe $2p_{3/2}$ XPS spectra, three peaks at ~709.1, 710.5 and 712.5 eV can be deconvoluted, which can be assigned to Fe^{2+} , octahedral Fe^{3+} and tetrahedral Fe^{3+} species [50,51], respectively. Compared to the fresh CuFe_2O_4 -SG-250 catalyst, the surface Fe^{2+} fraction of the photocatalytically reused catalyst kept nearly unchanged (~30%), whereas that of the thermocatalytically reused catalyst decreased to ~18%, implying that partial Fe_3O_4 in the fresh catalyst could be oxidized to Fe_2O_3 during the thermocatalytic OHA. As shown in Fig. 7(D), three types of surface oxygen species can be identified from the O 1s XPS spectra. The peaks at low BEs (529.5–529.8 eV), medium BEs (531.4–531.9 eV), and high BEs (533.0–533.5 eV) are ascribed to the lattice oxygen (O^{2-}), oxygen vacancies or surface adsorbed oxygen (O_2^- , O^- , OH) groups, and adsorbed water, respectively [52]. It is evident that the surface oxygen species increased after the reuse, with the O/(Cu+Fe) atomic ratio increasing from 1.5 to 3.0 for the thermocatalytically reused catalyst and to 5.0 for the photocatalytically reused catalyst. This is mainly due to the oxidation of CuNPs to Cu_2O and CuO during the OHA reactions. The increase of oxygen vacancies in the reused catalysts presumably implies that the surface adsorbed oxygen species may involve in the thermocatalytic and photocatalytic OHA.

To clarify the role of $\text{Cu}^0/\text{Cu}^+/\text{Cu}^{2+}$ species in CuFe_2O_4 -SG-250 for the OHA reactions, the Cu^0 powder, Cu_2O , CuO , $\text{Cu}/\text{Fe}_3\text{O}_4$ and Cu/TiO_2 were used as reference catalysts (Table 2). For the thermocatalytic OHA, CuO showed negligible activity, but Cu^0 powder showed even higher activity than Cu_2O . Given the induction period, the higher activity of Cu^0 powder can be due to the surface oxidized small-sized Cu_2O particles. Thus surface Cu^+ should be the predominant active site in thermocatalytic OHA, which is consistent with the previously reported $\text{CuO}_x/\text{TiO}_2$ and Cu_2O catalysts [24,53]. In contrast, Cu^0 is confirmed to be the active species in photocatalytic OHA by the facts that (1) Cu_2O and CuO are inactive, (2) freshly reduced $\text{Cu}/\text{Fe}_3\text{O}_4$, Cu/TiO_2 and CuFe_2O_4 -SG-250 samples show significantly higher activity in photocatalysis than in thermocatalysis. The CuFe_2O_4 -SG-250 showed much higher turnover

Table 2

Thermocatalytic and photocatalytic OHA reactions over reference copper catalysts.

Entry	Catalyst	Thermocatalytic OHA ^a		Photocatalytic OHA ^b	
		Yield ^c (%)	TON ^d	Yield ^c (%)	TON ^d
1	Cu^0	63	1.3	79	1.6
2	Cu_2O	25	0.5	<1	~0
3	CuO	2	<0.1	<1	~0
4 ^e	$\text{Cu}/\text{Fe}_3\text{O}_4$	61	6.1	75	7.5
5 ^e	Cu/TiO_2	57	5.7	72	7.2
6 ^e	CuFe_2O_4 -SG-250	65	6.5	83	8.3

Reaction conditions: phenylacetylene (0.2 mmol), *n*-dodecane (0.1 mmol) and catalyst with 50 mol% Cu in solvent (2 mL) with O_2 balloon.

^a Thermocatalytic OHA was carried out in DMSO at 120 °C for 5 h. ^b

Photocatalytic OHA was performed in ethanol with white LED irradiation (0.2 W/cm²) at ambient temperature (30 °C) for 5 h. ^c Yields were determined by GC. ^d Turnover number (TON) = (moles of converted phenylacetylene)/(moles of Cu). ^e Catalysts with 10 mol% Cu were used and reaction time was 5 h.

number (TON~8.3) than Cu^0 powder (TON~1.6), pointing to the beneficial effect of smaller CuNPs. Although bare TiO_2 could not absorb visible light, Cu/TiO_2 showed similar photocatalytic activity as $\text{Cu}/\text{Fe}_3\text{O}_4$ and CuFe_2O_4 -SG-250, suggesting that metallic CuNPs may act as the main light absorber in this white LED-induced photocatalysis. The TON achieved by the photocatalytic OHA over CuFe_2O_4 -SG-250 is comparable to the thermocatalytic OHA over various supported copper catalysts under ligand- and base-free conditions (Table S1). Interestingly, it is the first time to reveal that metallic Cu^0 can serve as active species for the heterogeneous photocatalytic OHA, which is clearly different from the previous report on the Cu^+ -based homogeneous photocatalytic OHA [30].

3.4. Influence of light source on heterogeneous photocatalytic OHA

It is known that the conduction electrons of the coinage (Cu, Ag and Au) metal nanoparticles can gain visible light energy through the localized surface plasmon resonance effect, which occurs when the frequency of incident photons matches that of these oscillating conduction band electrons in metallic nanoparticles [54–56]. Since the LSPR absorption peak of CuNPs appears at around 570 nm [33,34], the photoexcited hot electron-driven OHA reaction would be influenced by the light intensity and wavelength. Therefore, the dependence of the photocatalytic activity over CuFe_2O_4 -SG-250 on the light intensity and wavelength was investigated.

As shown in Fig. 8(A), the 1,3-diyne yield had an almost linear growth with the increase in light intensity of the white LED. The increased catalytic activity is likely due to the more energetic electrons generated at higher irradiation intensity. This linear relationship suggests that the photocatalytic OHA is first order in the incident photon and is dominated by a single photon absorption event [55]. Under LED light with wavelengths of 580–680, 480–580, 400–500 and 400–780 nm, the 1,3-diyne yield was 2%, 53%, 98% and 95% (Fig. 8(B)), respectively. Evidently, the red and green LED resulted in much lower pho-

Fig. 8. Dependence of catalytic activity of $\text{CuFe}_2\text{O}_4\text{-SG-250}$ for the photocatalytic oxidative homocoupling of phenylacetylene on the intensity (A) and wavelength (B) of the LED irradiation.

photocatalytic activity than the blue and white LED. The fact that the light in the wavelength range of 400–500 nm contributes to the highest white LED-induced conversion is consistent with the spectral range of the white LED (Fig. S2), in which the blue region shows the highest intensity. It is noteworthy that, except for metallic CuNPs, the other components (such as CuFe_2O_4 , Fe_3O_4 , Cu_2O and CuO) of $\text{CuFe}_2\text{O}_4\text{-SG-250}$ may also absorb visible light and contribute to the photocatalysis. To exclude the visible light absorption by the support, the dependence of the photocatalytic activity over Cu/TiO_2 on the light wavelength was also investigated (Fig. S3). The green LED resulted in more comparable conversion (52%) to the blue LED (65%) and white LED (76%), which underpins the primary contribution of the LSPR effect of CuNPs. When the heterogeneous photocatalytic OHA was conducted under natural sunlight (mean light intensity of 0.043 W/cm^2) instead of white LED at ambient temperature (about 30°C) for 8 h, moderate yield (63%) of 1,3-diyne was achieved. Although the detailed mechanism studies to clarify the nature of heterogeneous photocatalytic OHA are ongoing, the above findings reveal the possibility of using low-energy and -density light sources such as sunlight to drive the synthesis of 1,3-diynes on the CuNPs-based photocatalysts at ambient temperature under additive-free conditions.

3.5. Applicability and reusability of $\text{CuFe}_2\text{O}_4\text{-SG-250}$ catalyst

A series of heterogeneous thermocatalytic and photocatalytic OHA using various terminal alkynes were conducted to investigate the general applicability of the $\text{CuFe}_2\text{O}_4\text{-SG-250}$ catalyst (Table 3). Aromatic alkynes with electron-donating or electron-withdrawing substituents achieved high yield (>90%) towards the target 1,3-diyne products, with the photocatalytic efficiency comparable to the thermocatalysis. Nevertheless, $\text{CuFe}_2\text{O}_4\text{-SG-250}$ showed much lower activity in the photocatalysis than in the thermocatalysis for aliphatic alkynes. This is probably due to the fact that the aliphatic alkynes lack the large conjugated π -bonds like the substituted phenylacetylenes, thus the interaction between the alkyne and CuNPs is weakened and the substrate activation is more difficult and needs higher en-

Table 3

Thermocatalytic and photocatalytic oxidative homocoupling of various terminal alkynes to 1,3-diynes over $\text{CuFe}_2\text{O}_4\text{-SG-250}$ catalyst.

$$\text{R}-\text{C}\equiv\text{C}-\text{H} \xrightarrow[\text{DMSO, } 120^\circ\text{C} / \text{EtOH, LED, RT}]{\text{CuFe}_2\text{O}_4\text{-SG-250, O}_2} \text{R}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{R}$$

Entry	Alkyne	Thermocatalytic OHA ^a		Photocatalytic OHA ^b	
		Time (h)	Yield ^c (%)	Time (h)	Yield ^c (%)
1		3	90	3	95
2		6	98	6	98
3		6	98	8	98
4		8	93	8	96
5		9	97	10	98
6		3	77	10	83
7		3	81	10	40

Reaction conditions: phenylacetylene (0.2 mmol), *n*-dodecane (0.1 mmol), catalyst (20 mg), solvent (2 mL), O_2 balloon. ^a Thermocatalytic OHA was carried out in DMSO at 120°C . ^b Photocatalytic OHA was performed in ethanol with white LED irradiation (0.2 W/cm^2) at ambient temperature (30°C). ^c Yields were determined by GC and GC-MS on the basis of the conversion of alkynes. Selectivity in all cases was 100% to diynes.

ergy or longer reaction time.

To evaluate the reusability of $\text{CuFe}_2\text{O}_4\text{-SG-250}$, it was easily separated by a magnet, thoroughly washed by ethyl acetate and ethanol, dried and reused directly in the OHA reactions (Fig. 9). The $\text{CuFe}_2\text{O}_4\text{-SG-250}$ could be recycled and reused at least five times in the thermocatalytic OHA without drastic loss of activity, and the yield of 1,3-diyne decreased gradually from 90% to

Fig. 9. Reusability of the $\text{CuFe}_2\text{O}_4\text{-SG-250}$ and $\text{CuFe}_2\text{O}_4\text{-SG-300}$ catalysts in the thermocatalytic OHA and the $\text{CuFe}_2\text{O}_4\text{-SG-250}$ catalyst in the photocatalytic OHA.

77% after the fifth cycle. The stability of $\text{CuFe}_2\text{O}_4\text{-SG-250}$ is evidently better than the previously reported $\text{CuO}_x/\text{TiO}_2$ [24] and $\text{CuO}_x/\text{Fe}_3\text{O}_4$ [26] catalysts, and is also better than $\text{CuFe}_2\text{O}_4\text{-SG-300}$, which deactivated significantly with the yield decreasing from 95% to 23% after the fifth cycle. To clarify the surface Cu^+ fraction changes of $\text{CuFe}_2\text{O}_4\text{-SG-250}$ upon reuse, we performed further XPS analysis (Fig. S4). It is clear that the Cu^+ fraction decreased from 37% to 33% after the 1st cycle and to 28% after the 2nd cycle for the thermocatalytic OHA. Although the surface Cu^+ fraction decreased to 16% after the 5th cycle, the recycled catalyst was still efficient in the 6th cycle (~72% yield). Therefore, the activity is not in direct proportion to the Cu^+ fraction, because not all Cu^+ species are available for the reaction. Despite of the gradual decrease in the Cu^+ fraction, the surface Cu^+ species are sufficient to achieve a high activity upon reuse. As indicated by the results of element analysis for the fifth recycled catalysts, the gradual deactivation in the thermocatalytic OHA can be mainly due to the copper leaching, with the acid-dissolvable copper species decreasing from 22.5 to 6.3 wt% for the $\text{CuFe}_2\text{O}_4\text{-SG-300}$ and from 16.8 to 11.7 wt% for the $\text{CuFe}_2\text{O}_4\text{-SG-250}$. It is clear that the partial reduction of $\text{CuFe}_2\text{O}_4\text{-SG}$ spinel is more favorable than the complete reduction to enhance the stability of active copper species and retard the deactivation in the thermocatalytic OHA.

In contrast, the main reason for the deactivation in the photocatalytic OHA is not the copper leaching but the Cu^0 oxidation. Although the fresh $\text{CuFe}_2\text{O}_4\text{-SG-250}$ catalyst suffers drastic deactivation in the second photocatalytic cycle due to the oxidation of CuNPs as indicated by the XPS results (Fig. 7), the photocatalytic activity can be largely recovered by reducing the recycled catalyst with H_2 at 200 °C. By this H_2 pretreatment before the next cycle, $\text{CuFe}_2\text{O}_4\text{-SG-250}$ could be reused at least five times with the yield decreasing from 95% to 80% and the acid-dissolvable copper species decreasing from 16.8 to 13.8 wt% after the fifth cycle. Although it is more desirable to use a stable CuNPs catalyst in the photocatalytic OHA without the H_2 pretreatment before reuse, the interesting structure-performance relationship of $\text{CuFe}_2\text{O}_4\text{-SG-250}$ discussed above provide us a direction for future development of more efficient and stable CuNPs-based catalysts for the heterogeneous photocatalytic OHA.

4. Conclusions

We have shown that the prereduced copper-containing spinels can be used as effective heterogeneous catalysts for the thermocatalytic and photocatalytic oxidative homocoupling of terminal alkynes to conjugated 1,3-diynes. The magnetically separable CuFe_2O_4 shows the highest reducibility and has the most surface available copper species after H_2 reduction to achieve the highest catalytic activity for the OHA reactions. The sol-gel combustion method and the partial reduction at 250 °C can result in the optimal $\text{CuFe}_2\text{O}_4\text{-SG-250}$ catalyst showing high activity and stability. It is found that surface Cu^+ species is the active site for the thermocatalytic OHA and metallic CuNPs are the active sites for the photocatalysis. The LSPR effect of CuNPs contributes to the visible light-induced conversion and enables photocatalytic OHA at ambient temperature, which is more convenient and energy-saving than the thermocatalytic OHA at 120 °C. For the oxidative homocoupling of various aromatic alkynes, the photocatalytic efficiency is comparable to the thermocatalysis. The $\text{CuFe}_2\text{O}_4\text{-SG-250}$ catalyst can be magnetically separated and reused at least five times.

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Graphical Abstract

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On the comparable activity in plasmonic photocatalytic and thermocatalytic oxidative homocoupling of alkynes over prereduced copper ferrite

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A green and efficient heterogeneous photocatalytic oxidative homocoupling of alkynes under visible-light irradiation was developed, which exhibits comparable activity to thermocatalysis.

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预还原CuFe₂O₄在等离子体光催化及热催化炔烃氧化自偶联反应中具有可比活性的原因探究

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摘要: 面对能源短缺、环境污染的两大世界难题, 人们将更多的目光投向了清洁、可持续的绿色能源——太阳能。绿色高效的光催化转化被认为是替代传统热催化反应的最佳选择, 尤其是可见光催化。由Glaser首次提出的通过铜离子催化端基炔氧化自偶联(OHA)合成共轭1,3-二炔在天然产物、药物、光电子材料和聚合物合成中有着广泛的应用。但是传统的热催化OHA反应存在反应温度较高、需要添加含氮配体或碱性助剂、均相催化剂难以循环使用等问题。因此发展反应条件温和、无添加剂、可重复使用的多相光催化OHA反应体系势在必行。

鉴于Cu⁺物种被认为是多相热催化和均相光催化OHA中的活性物种, 以及我们研究组前期发展了多种表面富含Cu⁺物种的尖晶石材料, 我们提出了将这些含铜尖晶石应用于多相光催化OHA反应。研究发现, 只有预还原的含铜尖晶石才具有

可见光催化活性, 其中预还原 CuFe_2O_4 不仅在120 °C热催化OHA中表现出最高的催化活性, 其在室温可见光催化OHA中也具有最高的催化活性, 这主要是由于 CuFe_2O_4 具有较高的可还原性, 其在相同的还原温度300 °C下能获得最多的表面活性Cu物种. 因此, 我们进一步优化了 CuFe_2O_4 的制备方法和还原温度, 发现采用溶胶-凝胶燃烧法(SG)和250 °C部分还原所制备的 CuFe_2O_4 -SG-250催化剂具有更好的催化活性和稳定性, 在多种末端炔烃的热催化和光催化OHA中均获得了高于90%的1,3-二炔产率和能够与热催化相媲美的光催化活性.

由于未还原的 CuFe_2O_4 样品及单独 Fe_3O_4 在光催化和热催化OHA中均没有活性, 因此表面铜是活性位点. 为了探究铜物种的氧化态变化对催化活性的影响, 我们监测了1,3-二炔产率随反应时间的变化, 发现热催化有明显的诱导期而光催化没有. 通过反应前后XPS价态分析, 并结合 Cu^0 、 Cu_2O 和 CuO 作为参照催化剂的反应结果, 我们发现表面氧化的 Cu_2O 是热催化OHA的活性物种, 而金属铜纳米颗粒(CuNPs)是光催化OHA的活性位点. 结合UV-Vis光谱结果及不同强度和波长可见光对 CuFe_2O_4 -SG-250和 Cu/TiO_2 光催化性能影响的探究, 我们认为 CuNPs 的局域表面等离子体共振(LSPR)效应有助于可见光诱导的室温光催化OHA. 此外, 通过简单磁分离对 CuFe_2O_4 -SG-250的重复使用性进行了评估, 经过预还原处理该催化剂至少可重复使用5次. 显然, 本文为开发基于 CuNPs 的高效、绿色的多相可见光催化工艺, 以取代能源和污染密集型的铜基热催化反应提供了方向.

关键词: 炔烃; 氧化偶联; 铜铁尖晶石; 铜纳米颗粒; 表面等离子体共振

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