

Selective oxidation of aromatic alcohols to aldehydes catalyzed by HKUST-1-derived Cu-based carbon material and TEMPO

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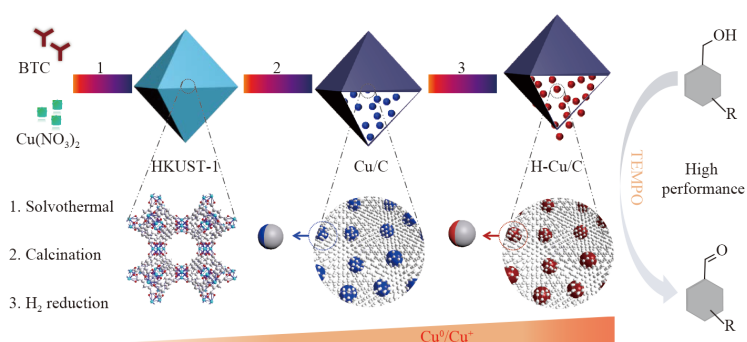
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Abstract: In this work, a Cu-based carbon catalyst (H-Cu/C) with an octahedral morphology was synthesized by pyrolyzing the metal-organic framework (MOF) precursor HKUST-1, where Cu(0) nanoparticles were uniformly dispersed in the carbon matrix, alongside the formation of island-like Cu₂O structures as the active sites. Multiple characterization techniques, including XPS, XRD, SEM and HRTEM, reveal the

critical role of carbon matrix in stabilizing the metal nanoparticles. In combination with TEMPO and using molecular oxygen as a green oxidant, the H-Cu/C catalyst is highly efficient in the selective oxidation of aromatic alcohols to the corresponding aldehydes under alkali-free conditions. Using benzyl alcohol as a model substrate, an alcohol conversion of 99.2% and a benzaldehyde yield of 94.1% were achieved under mild reaction conditions (100 °C, 0.5 MPa O₂, 1 h). The catalytic system displays excellent universality for various mono- and ortho/para-disubstituted aromatic alcohols, affording an alcohol conversion of over 99% and a yield of corresponding aromatic aldehydes of above 95%. In addition, the H-Cu/C catalyst can be regenerated *via* H₂ reduction and reused without significant loss of activity. This work provides a new strategy for designing green and efficient non-noble metal catalytic systems for the oxidation reactions.

Key words: metal-organic frameworks (MOFs); copper-based catalysts; selective oxidation; aromatic alcohols; TEMPO



The selective catalytic oxidation of alcohols (e.g., methanol, ethanol, biomass platform molecules) to value-added oxygenated chemicals is a pivotal process in organic synthesis^[1–5]. This transformation holds significant application potential in the anodic reactions of alcohol fuel cells, the upgrading of biomass-derived oxygenated fuels, and the green synthesis of fuel combustion precursors^[6–8]. Conventional oxidation methods, however, often rely on stoichiometric amounts of heavy metal salts (e.g., chromates, permanganates) or strong inorganic acids (e.g.,

nitric acid), which suffer from poor atom economy and generate substantial environmental pollutants due to the use of toxic and corrosive reagents, conflicting with the principles of green and sustainable energy chemistry^[9]. Consequently, developing novel catalytic systems utilizing molecular oxygen as a benign terminal oxidant is highly desirable. Such systems enable efficient alcohol conversion while avoiding the introduction and emission of hazardous substances, thereby promoting cleaner and more atom-economical fuel chemical processes with considerable

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scientific merit and broad application prospects.

The effective activation of the hydroxyl group and the removal of β -H and hydroxyl-H are key challenges in the catalytic oxidation of alcohols. Reported researches predominantly employ metals with excellent dehydrogenation properties as active components, primarily including noble metals (e.g., Pt, Au, Pd)^[10–11]. Although noble metal catalysts often exhibit high selectivity to target products in various alcohol oxidations, their intrinsic dehydrogenation capability is limited, frequently requiring the introduction of homogeneous bases as auxiliary additives to facilitate the reaction^[12]. Furthermore, the high cost and scarcity of noble metals restrict their large-scale industrial application. In contrast, the catalysts based on earth-abundant transition metals like Co and Cu are increasingly favored due to their lower cost, low toxicity, and absence of heavy metal pollution. However, these transition metals often exhibit weaker capability in activating substrates or interacting with molecular oxygen, thus typically necessitating higher metal loadings, bimetallic formulations, or basic additives/supports (e.g., NaOH, γ -Al₂O₃) to enhance their dehydrogenation performance^[13–14]. Therefore, designing a highly efficient and stable catalytic system capable of oxidizing alcohols to aldehydes under base-free conditions remains a significant challenge.

Our research has long been dedicated to the green oxidation synthesis, exploring hydrogen bonding effects, O₂ activation, and the regulation of metal coordination environments for efficient aerobic oxidation^[15–16]. Building upon this knowledge, we have now constructed a composite system comprising a MOF-derived copper-based carbon material and TEMPO for the efficient catalytic selective oxidation of aromatic alcohols to aromatic aldehydes under base-free conditions using molecular oxygen. Through controlled pyrolysis and reduction of the MOF precursor, a protective carbon matrix was formed, which can effectively inhibit the aggregation and deactivation of metal nanoparticles during the reaction and thereby maintain the stability and activity of the active sites throughout the catalytic cycle. Furthermore, this work elucidates the dynamic changes of different copper valence states during the selective oxidation, providing design insights for developing green and efficient non-noble metal catalytic systems in the oxidation reactions.

1 Experimental

1.1 Reagents and materials

Copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O), *N,N*-dimethylformamide (DMF), ethanol (EtOH), acetonitrile (CH₃CN) and benzyl alcohol (PhCH₂OH) were purchased from Tianjin Komio Chemical Reagent Co., Ltd. 1,3,5-benzenetricarboxylic acid (BTC, Ph(COOH)₃), *p*-methylbenzyl alcohol (C₈H₁₀O), *p*-chlorobenzyl alcohol

(C₇H₈OCl), benzaldehyde (PhCHO), *p*-methylbenzaldehyde (C₈H₈O), *p*-chlorobenzaldehyde (C₇H₆OCl), 5-hydroxymethylfurfural (5-HMF), 2-methoxybenzyl alcohol (C₈H₁₀O₂), *m*-bromobenzyl alcohol (C₇H₈OBr), 3,4-dimethoxybenzyl alcohol (C₉H₁₂O₃), 2-methoxybenzaldehyde (C₈H₈O₂), *m*-bromobenzaldehyde (C₇H₇OBr) and 3,4-dimethoxybenzaldehyde (C₉H₁₀O₃) were purchased from Aladdin Biochemical Technology Co., Ltd., J&K Scientific Ltd., or TCI (Shanghai) Development Co., Ltd. 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was purchased from J&K Scientific Ltd. Cinnamyl alcohol (C₉H₁₀O) and cinnamaldehyde (C₉H₈O) were obtained from Beijing Chemical Works and TCI, respectively. All chemicals were of analytical grade and used as received without further purification. Gases (O₂, N₂, H₂) with purity >99.999% were supplied by Dalian Kena Technology Development Co., Ltd.

1.2 Catalyst preparation

1.2.1 Synthesis of Cu-MOF (HKUST-1)

HKUST-1 was synthesized *via* a solvothermal method. Typically, 0.80 g of Cu(NO₃)₂·3H₂O was dissolved in a mixed solvent containing 70 mL of DMF, 4.7 mL of ethanol and 4.7 mL of deionized water. Then, 0.35 g of BTC was added, and the mixture was sonicated until complete dissolution. The resulting solution was transferred to a Teflon-lined stainless-steel autoclave and heated at 120 °C for 20 h. After cooling to room temperature, the precipitated brownish solid was collected by centrifugation and washed three times each with DMF and ethanol. The solid was then dried at 80 °C overnight to obtain HKUST-1. The phase purity of the product was verified by XRD, which agreed well with the reference pattern^[17].

1.2.2 Preparation of Cu/C

Approximately 0.30 g of as-synthesized HKUST-1 was placed in a quartz boat, which was then transferred to a quartz tube and positioned in a tube furnace. The tube was purged with high-purity N₂ to remove air. The temperature was raised to 800 °C at a heating rate of 10 °C/min under N₂ flow and maintained at 800 °C for 2 h. After pyrolysis, the sample was allowed to cool to room temperature under N₂ flow, yielding the catalyst denoted as Cu/C.

1.2.3 Preparation of H-Cu/C

Approximately 0.30 g of the Cu/C powder was placed in a quartz boat inside the tube furnace. The system was purged with N₂, then the gas was switched to high-purity H₂. The temperature was increased to 400 °C at 10 °C/min and held for 2 h under H₂ flow. Subsequently, the sample was cooled to room temperature under N₂ atmosphere,

yielding the reduced catalyst denoted as H-Cu/C.

1.2.4 Preparation of Cu/AC

Cu/AC was prepared *via* incipient wetness impregnation followed by carbothermal reduction. Briefly, 0.50 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (2.07 mmol) was dissolved in 1.5 mL of deionized water, and 1.00 g of activated carbon (AC) was added. The mixture was stirred thoroughly and left to impregnate overnight. After drying at 120 °C for 12 h, the resulting solid was ground. Approximately 0.30 g of this powder was pyrolyzed in a tube furnace under N_2 atmosphere at 600 °C for 2 h (heating rate: 10 °C/min), followed by cooling to room temperature under N_2 , yielding Cu/AC. This temperature was selected as the optimal pyrolysis temperature for Cu/AC to avoid excessive burn-off of the AC support and severe sintering of Cu particles at higher temperatures.

1.3 Material characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 spectrometer. X-ray powder diffraction (XRD) patterns were collected on a Rigaku D/Max 3400 diffractometer using $\text{Cu } K\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$), with a scanning range of 5°–80° (2 θ) and a scan rate of 5(°)/min. The average crystallite size was estimated using the Scherrer equation based on the full width at half maximum (FWHM) of the corresponding diffraction peaks. The morphology and microstructure of the samples were examined using a Quanta 200 FEG field emission scanning electron microscope (SEM) and a JEOL JEM-2000EX transmission electron microscope (TEM) operating at an accelerating voltage of 120 kV. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 409 PC/PG thermal analyzer under N_2 atmosphere from 35 to 700 °C at a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG ESCALAB MKII spectrometer using $\text{Al } K\alpha$ radiation to analyze the surface elemental composition and chemical states.

1.4 Catalytic activity evaluation

The catalytic oxidation reactions were performed in a 50 mL stainless steel autoclave equipped with a Teflon liner and a magnetic stirrer. In a typical procedure, benzyl alcohol (8 mmol, 0.34 g), the Cu-based catalyst (1% by mol relative to Cu), TEMPO (10% by mol), and acetonitrile (5 mL) were added to the reactor. The autoclave was sealed, heated to the desired temperature, and then pressurized with O_2 to 0.5 MPa. The reaction mixture was stirred vigorously, and timing commenced once the set temperature and

pressure were reached. The O_2 pressure was maintained at 0.5 MPa by periodic replenishment during the reaction. After the specified reaction time, the reactor was cooled to room temperature. The reaction mixture was quantitatively transferred to a volumetric flask, diluted with *n*-dodecane added as an internal standard, and analyzed using an Agilent 7890A/5975C gas chromatography-mass spectrometry (GC-MS) system equipped with an HP-5 MS capillary column and an EI ion source for qualitative and quantitative analysis.

2 Results and discussion

2.1 Structural characterization

The crystal structure and chemical composition of the synthesized samples were verified by FT-IR (Figure 1(a)) and XRD (Figure 1(b)), confirming the successful formation of HKUST-1. The characteristic diffraction peaks in the XRD pattern matched those of standard HKUST-1, and the characteristic absorption bands in the FT-IR spectrum were consistent with its functional groups^[17]. As shown in Figure 1(a), the FT-IR spectrum of BTC displayed absorption bands at 2500–3600 cm^{-1} and around 1720 cm^{-1} , attributable to O–H stretching and C=O stretching vibrations of the carboxylic acid groups, respectively. In the HKUST-1 precursor, these characteristic peaks of free carboxylic acids disappeared, replaced by bands corresponding to asymmetric and symmetric stretching vibrations of coordinated carboxylate groups, confirming successful metal-carboxylate coordination.

The changes during the pyrolysis and reduction stages were further investigated. TG-DSC analysis of HKUST-1 under N_2 atmosphere (Figure 1(c)) showed that the MOF framework decomposed at approximately 400 °C, accompanied by the gradual carbonization of organic components. This carbonization process likely involved the release of reducing gases (e.g., CO), which subsequently facilitated the carbothermal reduction of the metal nodes^[18].

The XRD characterization (Figure 1(d)) revealed that the pyrolysis of the well-defined HKUST-1 precursor at 800 °C resulted in a material containing primarily Cu_2O (Cu(I)) and Cu (Cu(0)) nanoparticles. Diffraction peaks at 43.4°, 50.6° and 74.2° were assigned to the (111), (200) and (220) crystal planes of Cu(0), respectively. Peaks at 36.4°, 42.3° and 61.3° corresponded to the (111), (200) and (220) crystal planes of Cu(I), respectively. The average crystallite size of Cu(0), estimated using the Scherrer equation based on the FWHM of the Cu (111) peak at 43.4°, was approximately 30 nm. After reducing the sample in H_2 at 400 °C for 2 h, the diffraction peaks corresponding to Cu(I) disappeared completely in the XRD pattern of H-Cu/C, leaving only the peaks for Cu(0), indicating the effective removal of the Cu(I) crystalline phase by H_2 reduction.

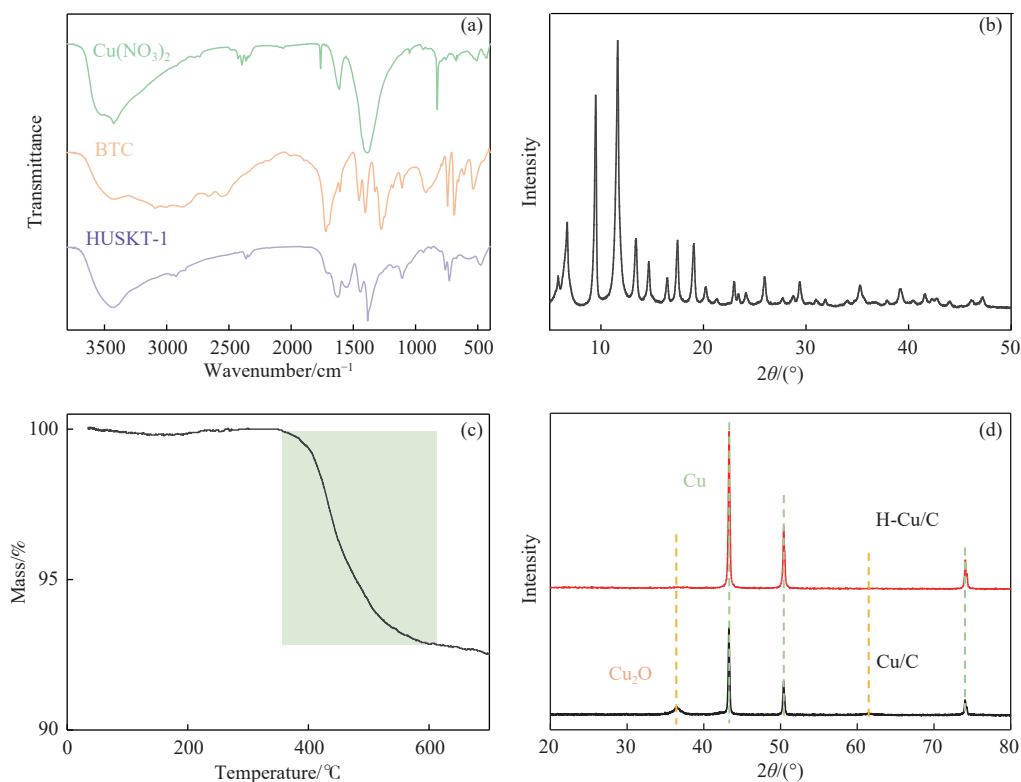


Fig. 1 (a) FT-IR spectra of Cu(NO₃)₂, BTC and HKUST-1; (b) XRD pattern of HKUST-1; (c) TG curve of HKUST-1 (in N₂ flow); (d) XRD patterns of Cu/C and H-Cu/C

The morphology of the H-Cu/C material was characterized by SEM and HRTEM. SEM images (Figure 2(a)–(c)) showed that the H-Cu/C catalyst, obtained after pyrolysis at 800 °C under N₂ followed by H₂ reduction at 400 °C, remained the regular octahedral morphology of the parent HKUST-1, with small granular protrusions visible on the surface. The TEM images (Figure 2(d)) confirmed that these protrusions were nanoparticles, most of which were dispersed in the carbon matrix, while a minority were directly

exposed. The average particle size was about 32 nm, consistent with the XRD results. At a higher magnification, HRTEM images (Figure 2(e)) clearly revealed that numerous Cu nanoparticles are uniformly dispersed within the conductive carbon matrix. Lattice fringes corresponding to the (111) plane of Cu(0) and the (111) plane of Cu(I) were clearly identifiable. Based on these observations, it is concluded that Cu(I) primarily exists as “island-like” domains on the surface of the copper nanoparticles (Figure 2(f)).

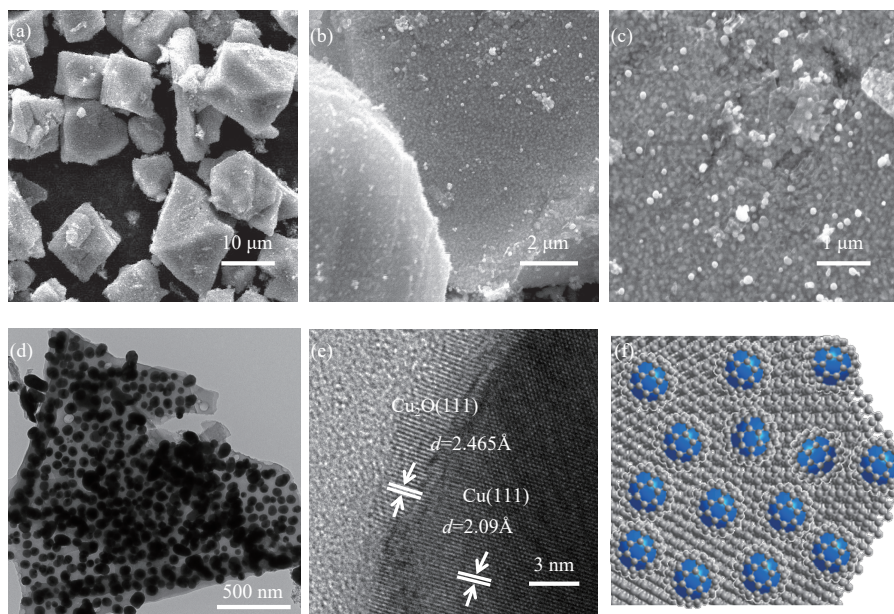


Fig. 2 (a)–(c) SEM images of H-Cu/C; (d) TEM image of H-Cu/C; (e) HRTEM image of H-Cu/C; (f) Graphic illustration of H-Cu/C

Moreover, the absence of significant agglomeration suggests a strong interaction between the metal species and the carbon framework derived from the MOF. This unique structure, where nanoparticles are dispersed and potentially confined by the carbon matrix, is believed to contribute to the enhanced catalytic performance and stability of H-Cu/C.

2.2 Catalytic performance evaluation

The performance of prepared catalysts was initially evaluated using benzyl alcohol as a model substrate and molecular oxygen as the oxidant. As shown in Figure 3, the composite catalytic system comprising H-Cu/C and TEMPO exhibited excellent activity and selectivity to aldehyde in the oxidation of benzyl alcohol. Under the conditions of 0.5 MPa O₂ and 100 °C for 1 h, an alcohol conversion of 99.2% and a benzaldehyde yield of 94.1% were achieved. In contrast, the system using the unreduced Cu/C catalyst combined with TEMPO afforded only 58.1% for the alcohol conversion and 56.7% for the aldehyde yield under identical conditions.

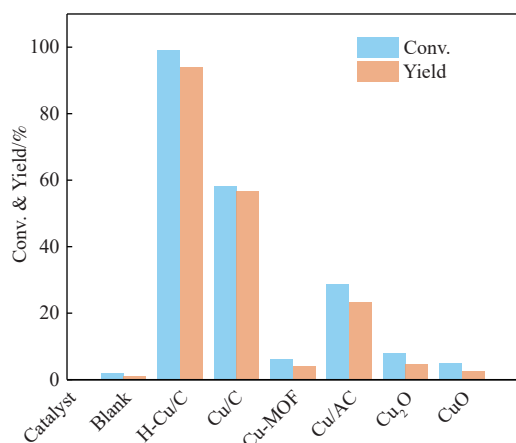


Fig. 3 Comparison of different Cu-based catalyst/TEMPO systems for the selective oxidation of PhCH₂OH
Reaction conditions: 8 mmol benzyl alcohol, 10% TEMPO, 5 mL of CH₃CN, 373 K, 0.5 MPa O₂, 1 h; Blank: no catalyst; Others: 1% catalyst.

Conversely, the combination of the non-pyrolyzed precursor HKUST-1 with TEMPO exhibited significantly reduced catalytic activity, yielding only 6.2% for the alcohol conversion and 4.2% for the aldehyde yield. Further investigation of the individual components showed that TEMPO alone gave merely 1.9% for the alcohol conversion and 1.0% for the aldehyde yield after reaction for 1 h. Similarly, laboratory-synthesized Cu₂O or CuO alone exhibited low activities, with the alcohol conversions of only 8.0% and 5.1%, respectively. These results underscore the crucial synergistic effect between the components in the composite system for achieving an efficient catalytic cycle.

2.3 Surface state analysis

Considering that heterogeneous catalysis primarily occurs at the catalyst surface^[19–21], XPS was employed to probe the surface chemical states of copper in the synthesized H-Cu/C, Cu/C and a spent H-Cu/C sample collected after 1 h of reaction (denoted as H-Cu/C-react-1h). XPS is highly surface-sensitive and provides information on the composition and structure of surface species^[22–24]. As shown in Figure 4(a), for the reduced H-Cu/C catalyst, only the Cu 2p_{1/2} (952.7 eV) and Cu 2p_{3/2} (932.8 eV) peaks were observed, while the characteristic satellite peak centered around 944.3 eV, typically associated with Cu²⁺ species, was absent, indicating the reduction of surface Cu(II) species to Cu(0) and/or Cu(I) during the H₂ treatment at 400 °C. Furthermore, the quantitative analysis of the Cu LMM Auger spectra (Figure 4(b)) revealed that the surface of the unreduced Cu/C catalyst comprised 71.2% Cu(I) and 28.8% Cu(II). After H₂ reduction, the surface composition of H-Cu/C was changed to 56.5% Cu(I) and 43.5% Cu(0), while Cu(II) was not detected. This demonstrated that H₂ reduction not only eliminated surface Cu(II) but also significantly increased the proportion of Cu(0), a key factor for the enhanced activity of H-Cu/C compared to Cu/C. In contrast, the surface valence state distribution of the H-Cu/C-react-1h sample reverted to a composition similar to that of the unreduced Cu/C, with Cu(II) content recovering to 36.2% and Cu(I) content decreasing to 63.8%, while Cu(0) was no longer detected.

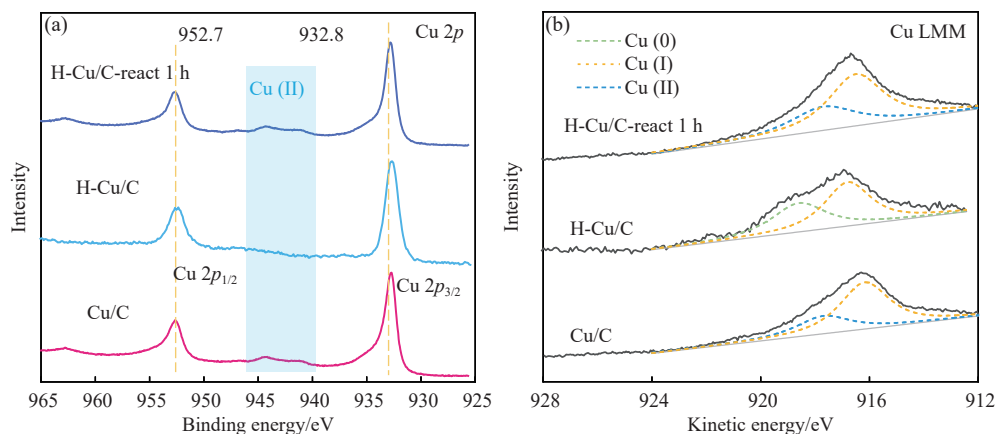


Fig. 4 (a) Cu 2p XPS spectra and (b) Cu LMM Auger spectra of Cu/C, H-Cu/C and H-Cu/C-react-1h

This phenomenon suggested that under the oxidative reaction conditions, part of the surface low-valence Cu(0) and Cu(I) species were re-oxidized to Cu(II). In addition, the catalyst regeneration experiments (discussed in Section 2.4) confirmed that the spent catalyst could recover its initial activity after H₂ reduction, further confirming the crucial role of reversible copper valence changes in the catalytic performance.

2.4 Identification of active sites and catalyst regeneration

To investigate the origin of the activity difference between H-Cu/C and Cu/C in benzyl alcohol oxidation and to monitor the transformation of copper species during the reaction, this study tested the time-activity curves of these two catalysts and analyzed samples at different reaction stages. As shown in Figure 5(a), during the initial 40 min, the formation rate of benzaldehyde on the H-Cu/C surface was approximately twice that on the Cu/C surface, indicating superior activity of H-Cu/C. The aforementioned XPS and Auger results clearly showed distinct initial surface copper valence distributions for H-Cu/C and Cu/C. To probe the bulk structural changes during the reaction, XRD was performed on H-Cu/C samples collected at different reaction times (Figure 5(b)). The fresh H-Cu/C catalyst only showed the diffraction peaks for the crystalline

Cu(0) phase, whereas Cu(II) or Cu(I) was not detectable. After 0.5 h of reaction, the characteristic peaks for Cu(I) emerged. At 1 h, even though benzyl alcohol was nearly completely converted, the catalyst bulk still consisted primarily of Cu(0) and Cu(I). However, upon prolonged reaction (e.g., 6 h), the intensity of the diffraction peaks for Cu(0) decreased significantly, while the Cu(I) peaks remained relatively stable and the peaks corresponding to Cu(II) eventually appeared. This suggests the progressive oxidation of the bulk Cu(0) during the extended reaction. Quantitative analysis of Auger spectra revealed that after reaction for 1 h, the proportion of Cu(0) on the surface decreased from 43.5% to 0, whereas the proportion of Cu(II) increased from 0 to 36.2%, and that of Cu(I) rose from 56.5% to 62.8%. These data suggest that during the reaction, part of the Cu(0) species is oxidized, contributing to the maintenance of the Cu(I) phase.

As the reaction time extended to 6 h, benzyl alcohol was completely converted, and the characteristic diffraction peaks for Cu(II) appeared in the XRD pattern, due to the redistribution and further oxidation of copper species. This may be attributed to the redistribution of copper species between the catalyst surface and bulk phase. To further investigate the effect of oxidative treatment, H-Cu/C was treated with O₂ (0.5 MPa) in acetonitrile solvent (10 mL) at different temperatures (80, 90 and 120 °C). As shown in Figure 5(c), molecular oxygen oxidized the copper species to varying degrees, forming Cu(II).

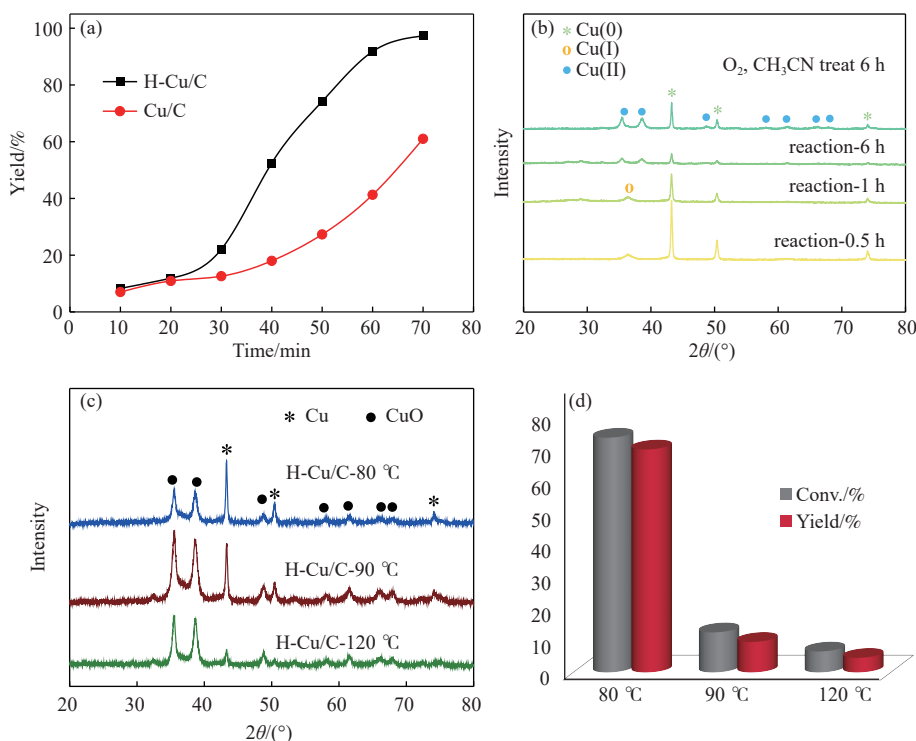


Fig. 5 (a) Time course for the selective oxidation of benzyl alcohol over Cu/C and H-Cu/C (reaction conditions: 8 mmol benzyl alcohol, 1% catalyst, 10% TEMPO, 5 mL of CH₃CN, 373 K, 0.5 MPa O₂); (b) XRD patterns of the catalysts collected at different reaction times and treated with oxygen; (c) XRD patterns of the catalysts treated with oxygen at different temperatures; (d) Performance of the catalysts treated with oxygen at different temperatures (reaction conditions: 8 mmol benzyl alcohol, 0.5% of catalysts, 10% of TEMPO, 5 mL of CH₃CN, 373 K, 0.5 MPa O₂)

The intensity of Cu(II) diffraction peaks increased with the treatment temperature, while the Cu(0) peaks weakened correspondingly, indicating that higher temperatures favor the formation of Cu(II). The catalytic performance of these oxygen-treated catalysts in benzyl alcohol oxidation varied significantly, as shown in Figure 5(d) (here the catalyst loading was decreased to 0.5% for a better comparison of the catalytic performance after treatment at different temperatures). The catalyst treated at 120 °C showed the lowest activity (6.6% conversion, 4.6% yield), whereas the sample treated at 90 °C exhibited slightly higher activity (12.6% conversion, 9.6% yield) and the catalyst treated at 80 °C retained partial activity (73.7% conversion, 70.0% yield). These results clearly demonstrated that the formation of a bulk Cu(II) crystalline phase was detrimental to the selective oxidation of benzyl alcohol. Combining the findings from Figure 5(b) and (c), it appeared that the presence of the substrate benzyl alcohol during the reaction

(before complete conversion) helps maintain the relative stability of the bulk Cu(0) phase, preventing its rapid transformation into the Cu(II) phase. In the absence of benzyl alcohol (or after its complete conversion), the bulk Cu(0) phase can be oxidized by oxygen to form Cu(II). This underscores the importance of Cu(0) crystalline phase in the Cu/C catalyst for achieving high activity and selectivity to aldehyde in the benzyl alcohol oxidation.

2.5 Catalytic mechanism and reusability

Although the copper components underwent oxidation during the reaction and the surface morphology of the metal particles became rougher after carrying out the reaction (SEM image, Figure 6(a)), the spent H-Cu/C catalyst could be regenerated *via* H₂ reduction.

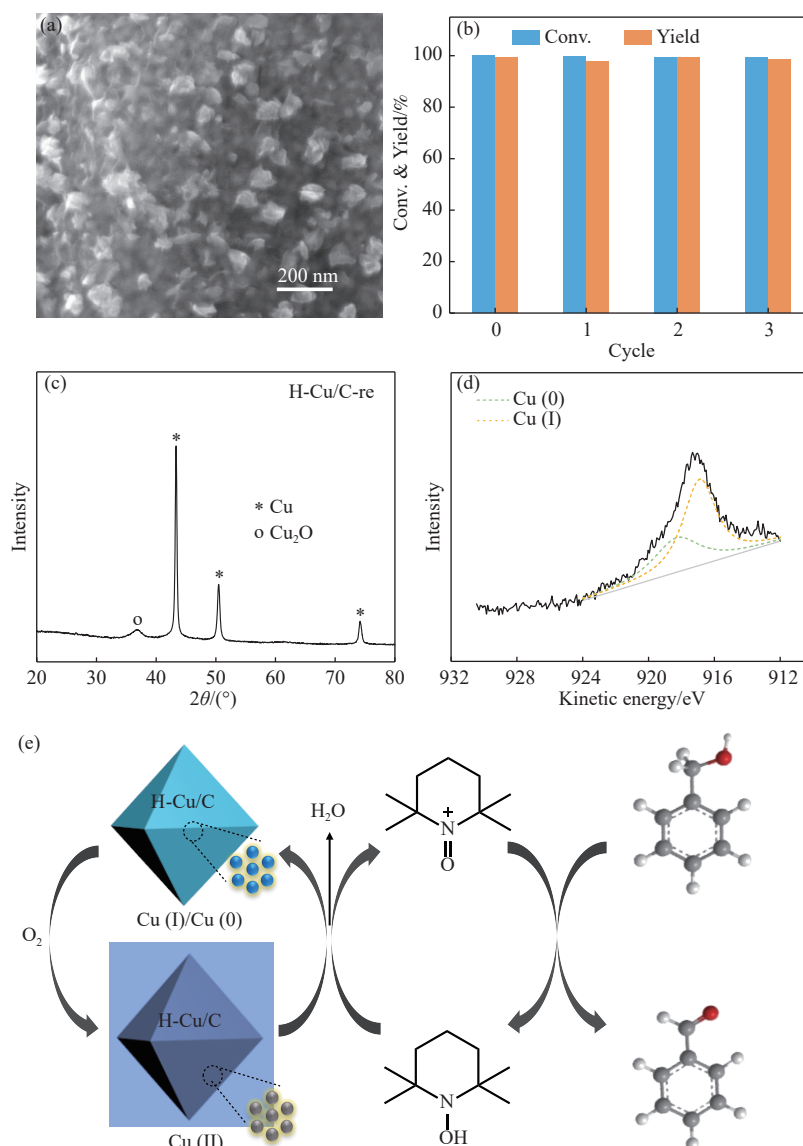


Fig. 6 (a) SEM image of H-Cu/C-reacted; (b) Recycle reactions for benzyl alcohol oxidation; (c) XRD pattern of H-Cu/C-re; (d) Cu LMM Auger spectrum of H-Cu/C-re; (e) Proposed mechanism for the oxidation of benzyl alcohol co-catalyzed by H-Cu/C and TEMPO

The regenerated catalyst (denoted H-Cu/C-re), when combined with TEMPO, exhibited performance comparable to that of the fresh catalyst in the selective oxidation of benzyl alcohol under the identical conditions. As shown in Figure 6(b), the benzaldehyde yield remained stable over three consecutive reaction cycles, demonstrating the good reusability of the catalytic system. The H-Cu/C-re displayed a significant enhancement of the Cu(0) diffraction peak in its XRD pattern (Figure 6(c)), accompanied by a decrease in the Cu(I) peak intensity, confirming the effectiveness of the regeneration process. Notably, a faint Cu(II) diffraction peak remained visible in XRD pattern of H-Cu/C-re, possibly due to incomplete reduction or slight surface oxidation during handling. Nevertheless, the performance of regenerated catalyst was nearly identical to that of the fresh catalyst, suggesting that trace amounts of Cu(II) have a negligible impact on the catalyst activity. Furthermore, Cu LMM Auger spectrum (Figure 6(d)) confirmed the absence of Cu(II) on the surface of H-Cu/C-re, with Cu(0) and Cu(I) proportions of 34.0% and 66.0%, respectively, close to the composition of the fresh catalyst. This further validated the H₂ reduction as an effective regeneration method for achieving copper valence reversibility and catalyst recyclability.

Based on the experimental results and the analysis of Cu valence changes in the fresh, spent and regenerated catalysts, a plausible reaction mechanism is proposed (Figure 6(e)): Cu(I) is oxidized by O₂ to generate Cu(II), with Cu(0) serving as an electron donor reservoir to maintain the concentration of Cu(I). Cu(II) then oxidizes TEMPO to the oxoammonium cation (TEMPO⁺). Subsequently, TEMPO⁺, as the key oxidizing species, directly oxidizes benzyl alcohol to benzaldehyde *via* a hydride transfer mechanism while converting itself to TEMPOH. TEMPOH is then re-oxidized to TEMPO by Cu(II), regenerating Cu(I) and closing the synergistic redox cycle. This mechanism is consistent with the widely accepted pathways for TEMPO-mediated oxidations under neutral conditions.

2.6 Substrate scope expansion

The H-Cu/C catalyst combined with TEMPO demonstrated excellent performance in the oxidation of a series of aromatic alcohols under base-free conditions (Figure 7). The catalytic system exhibited high activity and selectivity to aldehyde product for the oxidation of various substituted aromatic alcohols. For mono-substituted and ortho/para-disubstituted aromatic alcohols, the reactions achieved an alcohol conversion of > 99%, with corresponding aromatic aldehyde yields exceeding 95%. Specifically, the aldehyde yields for *p*-methylbenzyl alcohol, *p*-methoxybenzyl alcohol, *o*-methoxybenzyl alcohol and *p*-chlorobenzyl alcohol reached 97.4%, 99.0%, 95.2% and 98.8%, respectively, indicating the outstanding catalytic efficiency of H-Cu/C. The catalytic system was

also effective for structurally complex aromatic alcohols. For the oxidation of cinnamyl alcohol, the alcohol conversion exceeded 99% and the yield of cinnamaldehyde reached 94.9%. For the substrates with meta-substituents (e.g., *m*-bromobenzyl alcohol), the aldehyde yield decreased to 87.9%, as the electron-withdrawing effect of the benzene ring, affecting the stability of reaction intermediates and making them more prone to side reactions like over-oxidation or polymerization. When the benzene ring contained three substituents (e.g., 3,4-dimethoxybenzyl alcohol), the aldehyde yield dropped to 75.2%, primarily attributed to the steric hindrance of the multiple substituents that impeded the access of the alcohol hydroxyl group to the active sites on the catalyst surface. Despite the decreased yields, the alcohol conversions remained above 99%, indicating that this catalytic system retained good activity. Furthermore, in the oxidation of 5-hydroxymethylfurfural (HMF), the system achieved an alcohol conversion of 99% with a 2,5-diformylfuran (DFF) yield of 71.9%. The low DFF yield was inherent to the susceptibility of HMF to polymerization. Overall, this catalytic system shows excellent substrate generality for the selective oxidation of aromatic alcohols.

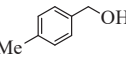
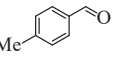
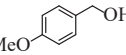
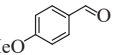
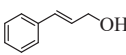
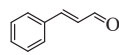
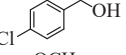
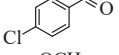
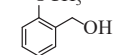
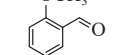
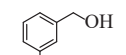
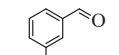
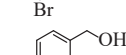
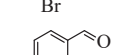
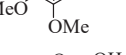
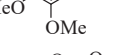
Entry	Substrates	Product	Conv./%	Yield/%
1			>99	97.4
2			>99	99.0
3			>99	94.9
4			>99	98.8
5			>99	95.2
6			>99	87.9
7			>99	75.2
8			>99	71.9

Fig. 7 Selective oxidation of aromatic alcohols to aromatic aldehydes catalyzed by H-Cu/C/TEMPO (reaction conditions: 8 mmol benzyl alcohol, 1% Cu catalyst, 10% TEMPO, 5 mL of CH₃CN, 373 K, 0.5 MPa O₂, 1 h)

3 Conclusion

In this study, a composite catalytic system was established by combining HKUST-1-derived copper-based carbon material (H-Cu/C) with TEMPO, which enabled the efficient and highly selective oxidation of aromatic alcohols using molecular oxygen as the oxidant under base-free

conditions. Through precise control of the pyrolysis process of HKUST-1 under an inert N₂ atmosphere, an H-Cu/C catalyst with a regular octahedral morphology was prepared. Structural characterization revealed that as the key features, the Cu nanoparticles uniformly dispersed in a carbon matrix and the unique island-like Cu₂O domains on the particle surface contributed to its high catalytic activity in the selective oxidation of aromatic alcohols. The H-Cu/C catalyst combined with TEMPO exhibited excellent catalytic performance in the selective oxidation of the model substrate benzyl alcohol, achieving an alcohol conversion of 99.2% and a benzaldehyde yield of 94.1%. The carbon matrix could effectively suppress the migration and sintering of metal nanoparticles during the reaction. The catalytic system demonstrated excellent universality towards a range of aromatic alcohol substrates bearing substituents with different electronic effects (e.g., electron-donating groups: -CH₃, -OCH₃; electron-withdrawing group: -Cl), achieving near-quantitative conversions and aromatic aldehyde yields above 95%. This work not only provides new insights into the design and controlled preparation of active sites in copper-based catalysts but also lays a catalytic foundation for developing green, efficient, and stable processes for the alcohol oxidation.

Declaration of Competing Interest

The authors declare no conflict of interest.

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HKUST-1 衍生的 Cu 基碳材料与 TEMPO 协同催化芳香醇 选择氧化制芳香醛

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摘 要:通过热解金属-有机框架(MOFs)前驱体 HKUST-1, 制备了一种具有八面体形貌的 Cu 基碳催化材料 H-Cu/C, 其碳基质表面中均匀分散着 Cu(0) 纳米颗粒, 并形成岛状 Cu₂O 活性位点。通过 XPS、XRD、SEM、TEM 等表征手段, 揭示了碳基质对 Cu 纳米颗粒的稳定作用。H-Cu/C 与 TEMPO 组成协同催化体系, 以分子氧为绿色氧化剂, 实现了在无碱条件下芳香醇高效高选择性催化氧化制备相应的芳香醛。以苯甲醇为模型底物, 在 100 °C 和 0.5 MPa O₂ 条件下反应 1 h, 苯甲醇转化率为 99.2%, 苯甲醛收率达到 94.1%。该催化体系对多种单取代和邻、对位双取代的芳香醇表现出优良的普适性, 获得了大于 99% 的醇转化率和超 95% 的芳香醛类产物收率, 且 H-Cu/C 催化剂经氢气还原再生后, 可重复使用。本研究为绿色、高效的非贵金属氧化催化体系设计提供了新思路。

关键词:金属-有机框架; 铜基催化剂; 选择氧化; 芳香醇; TEMPO

中图分类号: TB31

文献标识码: A

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