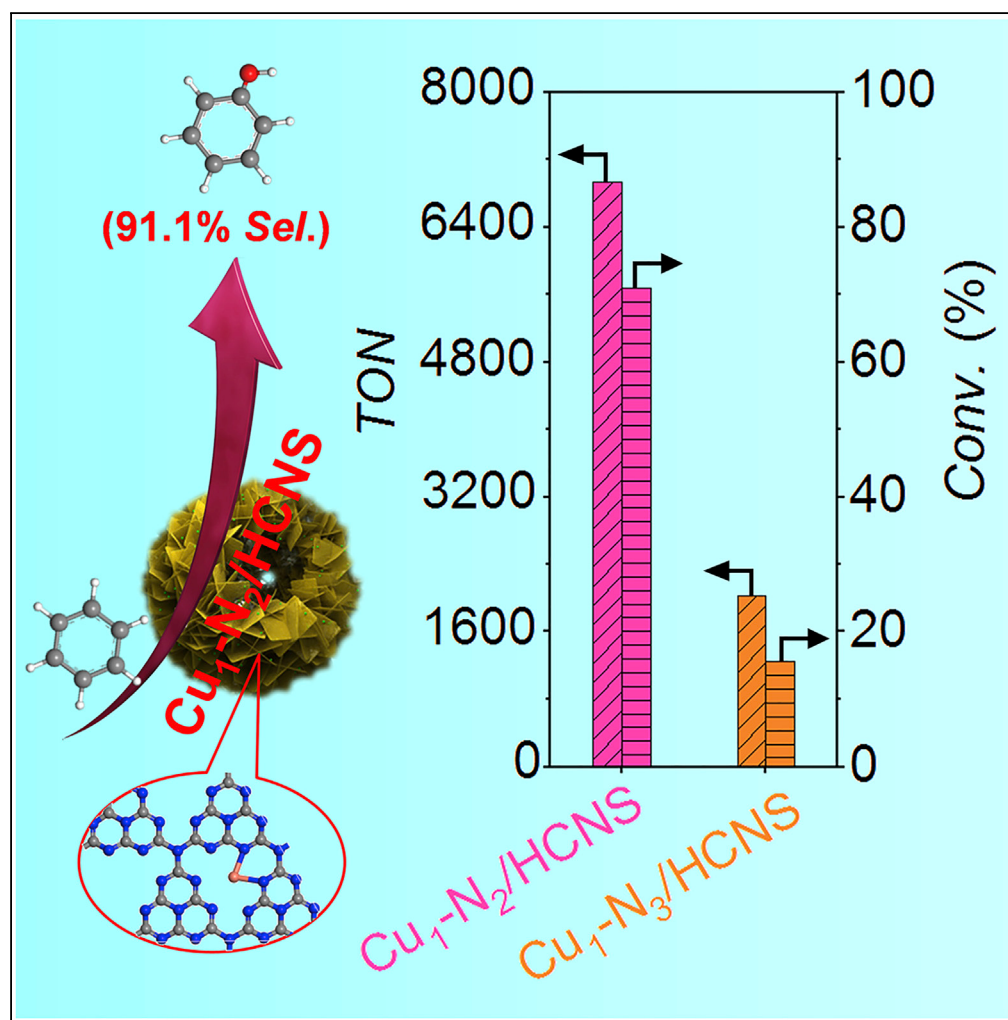


Article

Single Atomic Cu-N₂ Catalytic Sites for Highly Active and Selective Hydroxylation of Benzene to Phenol

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HIGHLIGHTS

Single-atom Cu catalyst
on HCNS with unique Cu-
N₂ moieties was
synthesized

Cu-N₂ shows 3.4 times
turnover number of Cu-N₃
for benzene hydroxylation

Unique Cu-N₂
coordination state leads
to lower energy barrier for
H₂O₂ activation

It paves a new avenue to
design single-atom
catalysts by tuning
coordination state

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Article

Single Atomic Cu-N₂ Catalytic Sites for Highly Active and Selective Hydroxylation of Benzene to Phenol

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SUMMARY

Searching for an efficient single-atom catalyst for benzene hydroxylation to phenol is of critical importance, but it still remains a challenge. Herein, a single-atom catalyst with unique Cu-N₂ moieties (Cu₁-N₂/HCNS) was prepared and confirmed by HAADF-STEM and EXAFS. Turnover number (TON) over Cu₁-N₂/HCNS (6,935) is 3.4 times of Cu₁-N₃/HCNS (2,034) under the same reaction conditions, and both exhibit much higher phenol selectivity (close to 99%) and stability compared with Cu nanoparticles and nanoclusters. Experiments and DFT calculations reveal that atomically dispersed Cu species are active sites for benzene hydroxylation to phenol, and the Cu-N₂ is more active than Cu-N₃ owing to its much lower energy barrier concerning the activation of H₂O₂ led by its unique coordination state of local atomic structure. We envision that this work opens a new window for modulating coordination environments of single metallic atoms in catalysis design.

INTRODUCTION

Activation of aromatic C-H bonds has been one of the most active research topics, yet long-standing challenge remains (Leitch and Frost, 2017; Sambiaro et al., 2018; Shan et al., 2018). Phenol is widely used as a versatile intermediate for phenolic resin, pharmaceuticals, agrochemicals, etc. (Bal et al., 2006; Wang et al., 2012). However, the current technology for phenol production by three-step cumene process generates large amounts of chemical waste and low-value by-product (Tsuji et al., 2017; Morimoto et al., 2015; Chen et al., 2009). Catalytic direct selective oxidation of benzene with H₂O₂ as oxidant is an acceptable pathway for efficient and clean phenol production (Ivanchikova et al., 2014; Su et al., 2017; Evtushok et al., 2018; Xia and Tang, 2012; Szécsényi et al., 2018). In this regard, heterogeneous catalytic hydroxylation of benzene with H₂O₂ to phenol is highly desirable (Zhang et al., 2017a, 2017b; Deng et al., 2015; Zhu et al., 2018; Yang et al., 2013; ElMetwally et al., 2018; Han et al., 2017). Although numerous efforts of designing such catalytic system have been made and considerable achievements have been obtained, it still remains a challenge (Balducci et al., 2003). Nitrogen-doped carbon materials have been found to be active for hydroxylation of benzene with H₂O₂ under mild condition yet shows low catalytic activity (Yang et al., 2013). Metal-doped carbon nitride shows an improved activity for hydroxylation of benzene with H₂O₂ to phenol but still remains unsatisfactory (Chen et al., 2009; Di et al., 2010; Xu et al., 2018; Zhang et al., 2018a, 2018b; Hosseini et al., 2018). Therefore, developing efficient catalysts for benzene hydroxylation with H₂O₂ to phenol is of great urgency.

Owing to enhanced intrinsic activity and selectivity toward targeted product and maximized utility of metal atoms (Dvořák et al., 2016; Kwon et al., 2017; Chen et al., 2018a, 2018b; Yamaguchi et al., 2017; Li et al., 2018a, 2018b; Malonzo et al., 2016; Liang et al., 2015), single-atom catalyst (SAC) has been emerging as an attractive frontier in heterogeneous catalysis (Qiao et al., 2011; Mitchell et al., 2018; Chen et al., 2018a, 2018b; Thomas et al., 2005; Yamashita et al., 2018). Up to now, SAC has been broadly applied to thermo-, electro-, and photo-catalysis owing to its extraordinary catalytic performance from the unique electronic properties of single atomic sites (Zhang et al., 2018a, 2018b; Gao et al., 2016; bin Mohd Yusoff et al., 2015; Yang et al., 2016; Cheng et al., 2018). Especially for the activation of C-H bonds, SAC shows extraordinary catalysis than nanoparticles (Marcinkowski et al., 2018; Yuan et al., 2018; Yamaguchi et al., 2018). Single-atom Fe/Ni/Co materials are proved to be efficient for benzene hydroxylation with H₂O₂ to phenol (Ivanchikova et al., 2014; Su et al., 2017; Evtushok et al., 2018; Wang et al., 2015). However, the activity and selectivity are far from their applications. Our previous work shows that single atomic Cu-N₃ sites

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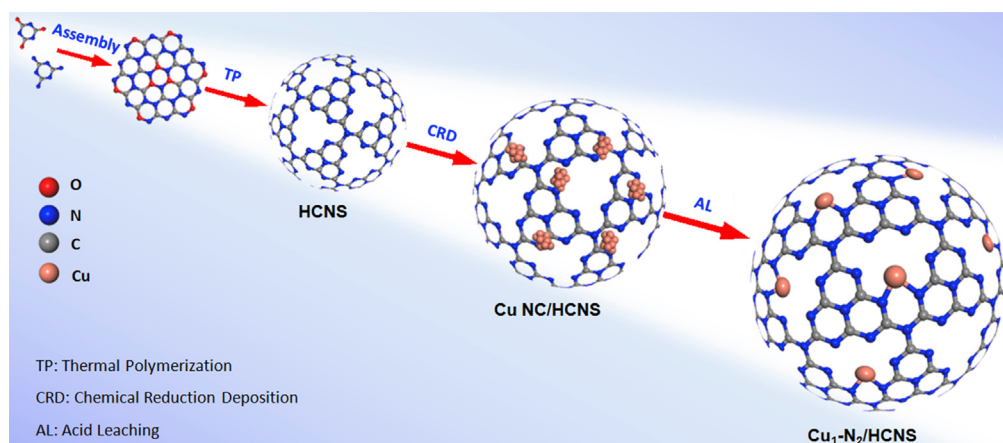
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Scheme 1. Schematic Illustration of the Preparation of Single-Atom Cu₁-N₂/HCNS Catalyst

have extraordinary phenol selectivity with H₂O₂ as oxidant, yet the activity still remains to be improved (Zhang et al., 2018a, 2018b). Therefore, developing single-atomic Cu catalysts with increased activity for benzene hydroxylation with H₂O₂ is desirable. In homogeneous catalysis, the design of ligands plays crucial roles in tuning activity by modulating the coordination states of central metal atoms (Morimoto et al., 2015). Also for heterogeneous catalysis, as reported by references Evtushok et al., 2018; Liu et al., 2017; Jiang et al., 2018; Han et al., 2018, the coordination states of metal atom in SAC significantly affect the catalytic performance. Considering this, modulating coordinated state of single-atom Cu-N_x moieties on hollow carbon nitride microsphere (HCNS) can be a sapiential approach to develop an excellent single-atom catalyst for benzene hydroxylation to phenol.

Herein, a single-atom Cu catalyst isolated on HCNS with unique Cu-N₂ moieties (Cu₁-N₂/HCNS) has been successfully prepared by a facile chemical reduction deposition-acid leaching (CRD-AL) method (see Scheme 1), confirmed by extended X-ray absorption fine structure (EXAFS) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Surprisingly, Cu₁-N₂/HCNS exhibits 3.4 times turnover number (TON) (6,935) of Cu₁-N₃/HCNS (2,034) toward benzene hydroxylation to phenol; besides, both single-atom catalysts demonstrate much higher selectivity and stability than Cu nanoparticles or nanoclusters. HAADF-STEM, EXAFS, and kinetic results reveal that the single-atom Cu species are catalytic active sites for benzene hydroxylation to phenol and Cu-N₂ is extremely more active than Cu-N₃ owing to its unique local atomic structure.

RESULTS AND DISCUSSION

Synthesis and Characterization of Cu₁-N₂/HCNS Catalyst

In this paper, a single-atom Cu catalyst isolated on HCNS with unique Cu-N₂ moieties (Cu₁-N₂/HCNS) has been successfully prepared by a facile CRD-AL method. Typically, 0.14 g of HCNS carrier (Jun et al., 2013a, 2013b) was first ultrasonically dispersed in 20 mL of Cu(NO₃)₂ aqueous solution (2 mmol L⁻¹). Then, the Cu species were deposited on HCNS surface with 1 mL of NaBH₄ (0.5 mol L⁻¹) as reductant. After stirring for 4 h at room temperature, solid sample was collected by centrifugation and washed with DI water and ethanol three times, respectively. Subsequently, the solid sample was dried at 60°C for 12 h. For now, the obtained dry solid catalyst is denoted as Cu NC/HCNS (1.14 wt% Cu, inductively coupled plasma-atomic emission spectrometry [ICP-AES]). To get single-atom catalyst Cu₁-N₂/HCNS, 0.01 g of Cu NC/HCNS was further treated with 10 mL of dilute HNO₃ solution for 4 h at room temperature. The solid was centrifuged, washed with DI water to neutral and dried at 60°C for 4 h. The finally acquired solid catalyst was named as Cu₁-N₂/HCNS (0.23 wt% Cu, ICP-AES). During the acid-leaching process, the CuO nanoclusters are easily eliminated, whereas the single atoms anchored by the support are stable (Liu et al., 2018). Although metallic Cu can be oxidized, in our synthetic system with massive excess NaBH₄, the Cu²⁺ captured by N atoms on HCNS can be *in situ* reduced and single-atomic Cu coordinated with neighboring N atoms formed. The method applied in this work is different from the pre-assembly method for Cu-N₃ in our former report (Zhang et al., 2018a, 2018b). For Cu₁-N₂/HCNS catalyst, the Cu species were deposited on the pre-formed HCNS, followed by

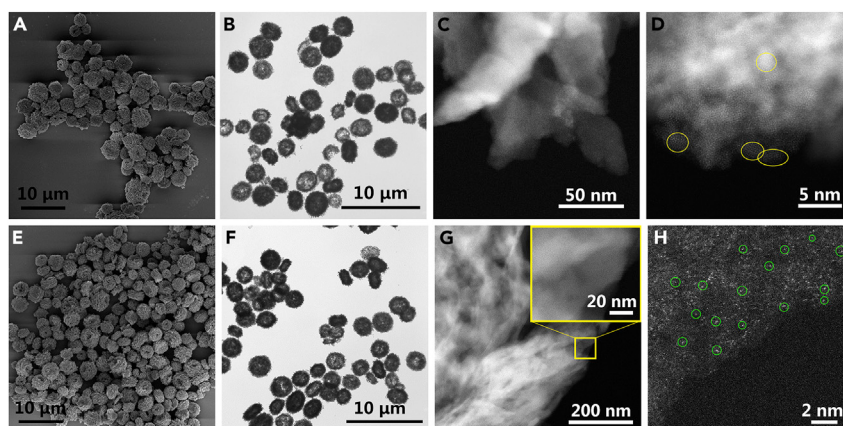


Figure 1. Characterization of As-prepared Samples

(A and B) Scanning electron microscopy (SEM) (A) and transmission electron microscopy (TEM) (B) images of Cu NC/HCNS catalyst.

(C and D) HAADF-STEM images of Cu NC/HCNS catalyst, the Cu clusters are highlighted by yellow circles.

(E and F) SEM (E) and TEM (F) images of Cu₁-N₂/HCNS catalyst.

(G and H) HAADF-STEM images of Cu₁-N₂/HCNS catalyst, the single Cu atoms are highlighted by green circles.

acid-leaching treatment; CuO_x clusters were removed while the single-atomic Cu was anchored by two neighboring N atoms and formed the Cu-N₂ sites, whereas for the Cu₁-N₃/HCNS catalyst, the Cu²⁺ ions were pre-coordinated with melamine to form Cu-Mel complex and the Cu atoms were isolated in the supermolecular assemblies; subsequently, Cu-N₃ sites were *in situ* formed during thermal polymerization.

X-ray powder diffraction (XRD) patterns of Cu NC/HCNS and Cu₁-N₂/HCNS catalysts (see Figure S1) display the characteristic peaks at 12.9° and 27.4°, assigned to (100) and (200) crystal faces of g-C₃N₄, respectively (Zhao et al., 2018), indicating deposition and acid leaching have no influence on the crystal property of g-C₃N₄ support. Field emission scanning electron microscopy and transmission electron microscopy (see Figures 1A, 1B, 1E, 1F, and S2A) are applied for characterization toward the morphology of as-prepared catalysts. It is shown that Cu₁-N₂/HCNS and Cu NC/HCNS catalysts feature a regular hollow spherical structure (Zhang et al., 2018a, 2018b; Jun et al., 2013a, 2013b). Textural properties (see Figure S3 and Table S1) indicate that the micro-structure of HCNS is maintained after loading Cu atoms. The porous hollow micro-/nano-structures have benefit for the catalytic reaction by improving accessibility of catalytic sites to reactants (Zhang et al., 2018a, 2018b; Harmer et al., 1996; Matei et al., 2013; Li et al., 2018a, 2018b). Furthermore, the textural properties of CN₁-N₂/HCNS and Cu₁-N₃/HCNS are similar. Also, our former research indicates that the elemental composition of Cu₁-N₃/HCNS is same as the HCNS support (molar ratio of N/C = 1.5) (Zhang et al., 2018a, 2018b). The addition of trace Cu-melamine complex (0.85 wt% Cu in the final Cu₁-N₃/HCNS catalyst) shows inconspicuous effect on the textural properties of Cu₁-N₃/HCNS catalyst compared with the HCNS support.

For further observation of metal species dispersed on g-C₃N₄ support, HAADF-STEM experiments were performed and the obtained images are displayed in Figures 1C, 1D, 1G, and 1H. No obvious metallic nanoparticles can be observed both on Cu NC/HCNS and Cu₁-N₂/HCNS. XRD patterns (see Figure S1) also exhibit no characteristic peak corresponding to Cu nanoparticles. However, HAADF-STEM image (see Figure 1D) of Cu NC/HCNS displays the existence of nanoclusters less than 2 nm. The fitting results (see Table S2) toward R-space EXAFS spectrum (see Figure S4) of Cu NC/HCNS are matched well with CuO_x clusters, i.e., first shell of Cu-O at 1.92 Å with CN = 2.9 and second shell of Cu-Cu (originated from Cu-O-Cu) at 2.87 Å with 0.4 of coordination (CN). Besides, X-ray photoelectron spectroscopy (XPS) of O 1s spectrum (see Figure S5A) reveals the existence of lattice O²⁻ species and the N 1s XPS spectrum (see Figure S5B) displays no obvious peak assigned to Cu-N species, further proving the CuO_x clusters on the Cu NC/HCNS. For clear observation, the raw and enlarged image of Figure 1D is given in Figure S2B. Concerning Cu₁-N₂/HCNS catalyst, single Cu atoms are clearly identified as bright spots (highlighted by green circles) isolated on g-C₃N₄ surface by HAADF-STEM image (see Figure 1H). The Cu content of Cu₁-N₂/HCNS is ca. 0.23 wt% determined by inductively coupled plasma-atomic emission spectroscopy.

The amount of active Cu sites in single-atom Cu₁-N₂/HCNS catalyst is determined by KSCN titration method, and the results are shown in Figure S6. The result indicates that, for Cu₁-N₂/HCNS catalyst, about 80% of the loaded Cu atoms serve as active sites (0.029 mmol_{Cu}/g_{Cat.}) (see Figure S6A), whereas for Cu₁-N₃/HCNS, about 60% of the loaded Cu atoms serve as active sites (0.080 mmol_{Cu}/g_{Cat.}) (see Figure S6B).

Heteroatom, like N atoms, in carbon matrix have been proved to be efficient anchoring sites for stabilizing metal atoms (Zhang et al., 2018a, 2018b; Liu et al., 2018; Qu et al., 2018). g-C₃N₄ features abundant N content and chemical stability (Liu et al., 2016) and, therefore, has been considered as an ideal support for single-atom catalysts (Zhang et al., 2018a, 2018b). For understanding the electronic character of the developed Cu₁-N₂/HCNS catalyst, X-ray photoelectron spectroscopy (XPS) was carried out (see Figures 2 and S7). XPS survey spectrum of Cu₁-N₂/HCNS (see Figure S7A) displays the characteristic peaks of C, N, O, and Cu. The deconvoluted O 1s spectrum (see Figure 2A) shows no lattice O²⁻ species, proving the complete etching of Cu_xO clusters. C 1s spectrum (see Figure S7B) reveals the major content of C-C, N-C=N species, whereas the deconvoluted N 1s spectrum of Cu₁-N₂/HCNS (see Figure 2B) features an extra peak (399.0 eV) assigned to Cu-N species (Zhang et al., 2017a, 2017b), besides the characteristic peaks belonging to pyridinic-N (398.5 eV), pyrrolic-N (400.1 eV), and graphitic-N (401.0 eV) compared with HCNS matrix. The strong coordination of Cu atom with surrounding N atoms in the g-C₃N₄ matrix stabilizes the atomically dispersed Cu sites. Cu 2p XPS spectra (see Figure 2C) show that the characteristic peak of Cu⁺ 2p_{3/2} shifts to 932.8 eV in single-atom Cu₁-N₂/HCNS compared with that of Cu NC/HCNS, further confirming the strong interaction between single Cu atoms and the g-C₃N₄ matrix.

To further investigate the electronic properties and coordination environment of Cu₁-N₂/HCNS, X-ray absorption near-edge spectroscopy (XANES) and EXAFS measurements were performed. Cu K-edge XANES profiles for the measured sample and the related references (Cu foil, Cu₂O, and CuO) are shown in Figure 2D. Cu₁-N₂/HCNS exhibits an energy absorption edge between Cu⁺ (Cu₂O) and Cu²⁺ (CuO) standards in the range of E₀ (around 8,979 eV), and the corresponding oxidation state of copper is determined as +1.5 via linear combination fitting (Frenkel et al., 2011). This observation agrees with the related XPS results (see Figure 2C). EXAFS spectra (see Figure 2E) for Cu₁-N₂/HCNS only displays a prominent peak at approximately 1.9 Å, and no significant contribution for metallic Cu or oxidized CuO_x clusters at longer distances above 2.5 Å is observed, revealing the atomic dispersion of isolated Cu atoms throughout HCNS matrix. XANES is the nowadays the most direct and efficient technology for the characterization concerning atomic structure of single-atom catalyst. The XANES spectra of central atoms with different coordination numbers or ligands usually display distinct difference in adsorption curves (Kau et al., 1987; Sorrell and Malachowski, 1983; Sorrell et al., 1982). The near-edge of Cu₁-N₂/HCNS and Cu₁-N₃/HCNS (see Figure 2F) features obviously different shapes, implying the possible difference in coordination environment of single-atom Cu moieties. The Cu K-edge spectrum of Cu₁-N₂/HCNS is similar to that of the compound Cu(pze)BF₄, in which the central Cu ion is coordinated with N₂O-ligation (Kau et al., 1987; Sorrell and Malachowski, 1983). However, Cu₁-N₃/HCNS catalyst shows a similar Cu K-edge spectrum to compound [Cu₂(mxyN₆)](BF₄)₂, in which the central Cu ion is coordinated with N₃-ligation (Kau et al., 1987; Sorrell et al., 1982). This difference in the adsorption curve of XANES spectra indicates that the local atomic structure of single Cu atoms over Cu₁-N₂/HCNS differs from that over Cu₁-N₃/HCNS. To further obtain the structural parameters of copper in Cu₁-N₂/HCNS, we conducted EXAFS fitting in R space (see Figure 2G) via a possible structural model presented in Figure 2I. Two nitrogen atoms are coordinated with isolated copper center, which is also capped by adsorbed oxygen-containing molecule (O₂ and/or H₂O and/or CO₂) to form saturated structure for its stable existence. Table S3 shows that the bond length of Cu-N is determined to be 1.92 Å, plus a minor Cu-O shell at 1.96 Å with the coordination number of ca. 1. All these results are well consistent with the hypothesized structural model (see Figure 2I) in the density functional theory (DFT) calculation. For comparison of the reaction mechanism of H₂O₂ activation over Cu₁-N₂/HCNS and Cu₁-N₃/HCNS, the structure model of Cu-N₃ has been constructed and optimized via DFT according to the EXAS fitting results (see Figures 2F, S4D, and S4E and Table S2) and displayed in Figures 2H and 2J.

Catalytic Evaluation

As a critically important chemical transformation, aromatic C-H bond activation has been one of the most active research topics (Morimoto et al., 2015; Marcinkowski et al., 2018; Shilov and Shul'pin, 1997; Labinger and Bercaw, 2002; Wencel-Delord; Glorius, 2013). Herein, benzene hydroxylation with H₂O₂ to phenol was performed as a model reaction to evaluate the catalytic performance of the developed Cu₁-N₂/HCNS catalyst (see Figure 3 and Table S4). For comparison, Cu NC/HCNS, Cu NP/HCNS, and our previously reported

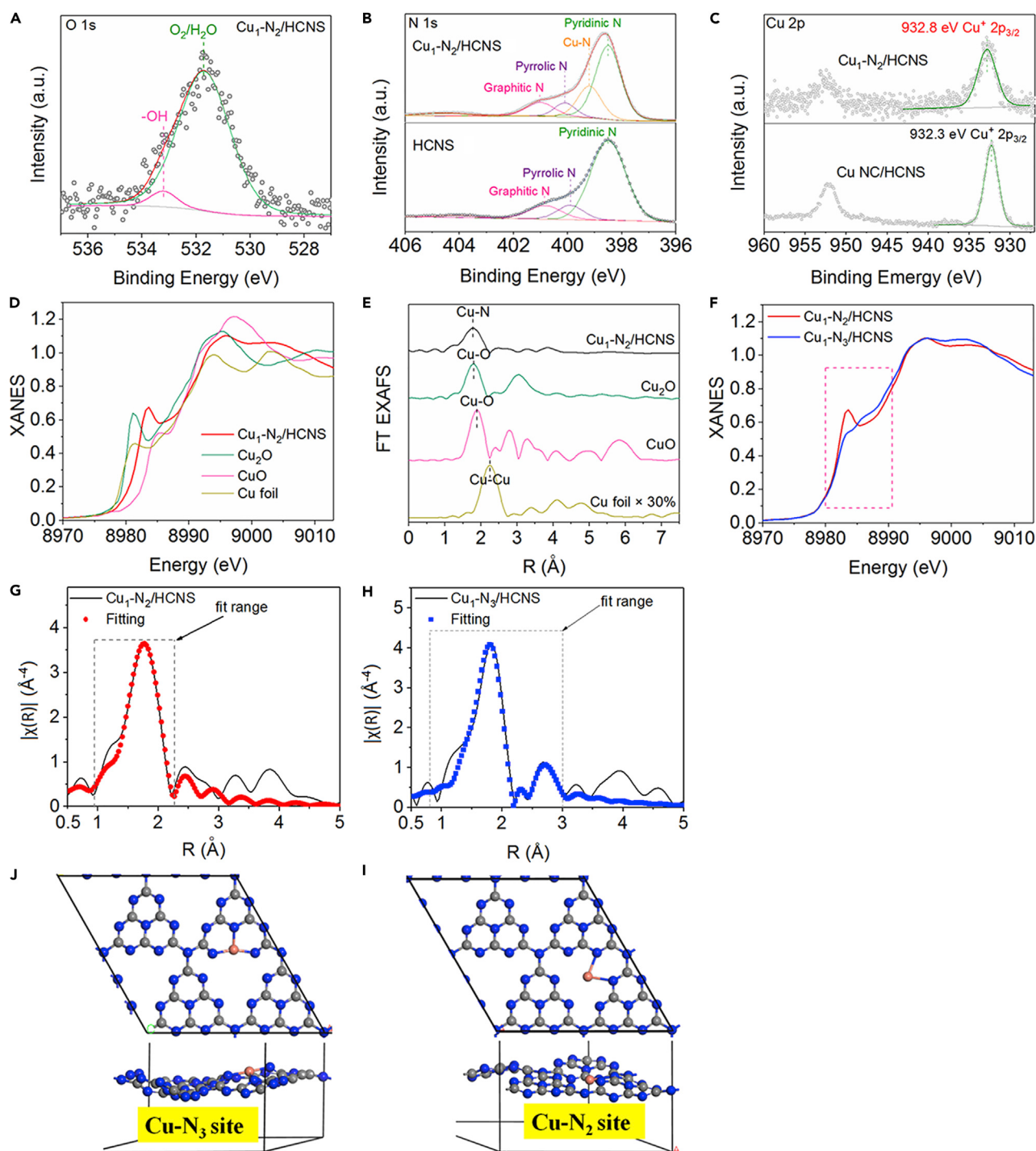


Figure 2. X-Ray Spectroscopy Analyses of single-atom catalyst

(A) The O 1s XPS spectrum of $\text{Cu}_1\text{-N}_2/\text{HCNS}$ single-atom catalyst.

(B) The N 1s XPS spectra of single-atom $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst and HCNS support.

(C) Cu 2p XPS spectra of $\text{Cu}_1\text{-N}_2/\text{HCNS}$ single-atom catalyst and Cu NC/HCNS nanocluster catalyst.

(D and E) Normalized Cu K-edge XANES spectra (D) and k^3 -weighted Fourier transform spectra (E) from Cu K-edge EXAFS of Cu foil, CuO , Cu_2O , and $\text{Cu}_1\text{-N}_2/\text{HCNS}$.

(F) The comparison of normalized Cu K-edge XANES spectra of $\text{Cu}_1\text{-N}_2/\text{HCNS}$ and $\text{Cu}_1\text{-N}_3/\text{HCNS}$ (Zhang et al., 2018a, 2018b).

(G and H) The corresponding EXAFS fitting curves of $\text{Cu}_1\text{-N}_2/\text{HCNS}$ (G) and $\text{Cu}_1\text{-N}_3/\text{HCNS}$ (H).

(I and J) The models of Cu-N_2 sites in $\text{Cu}_1\text{-N}_2/\text{HCNS}$ (I) and the model of Cu-N_3 sites in $\text{Cu}_1\text{-N}_3/\text{HCNS}$ (J), orange, Cu; gray, C; blue, N; red, O.

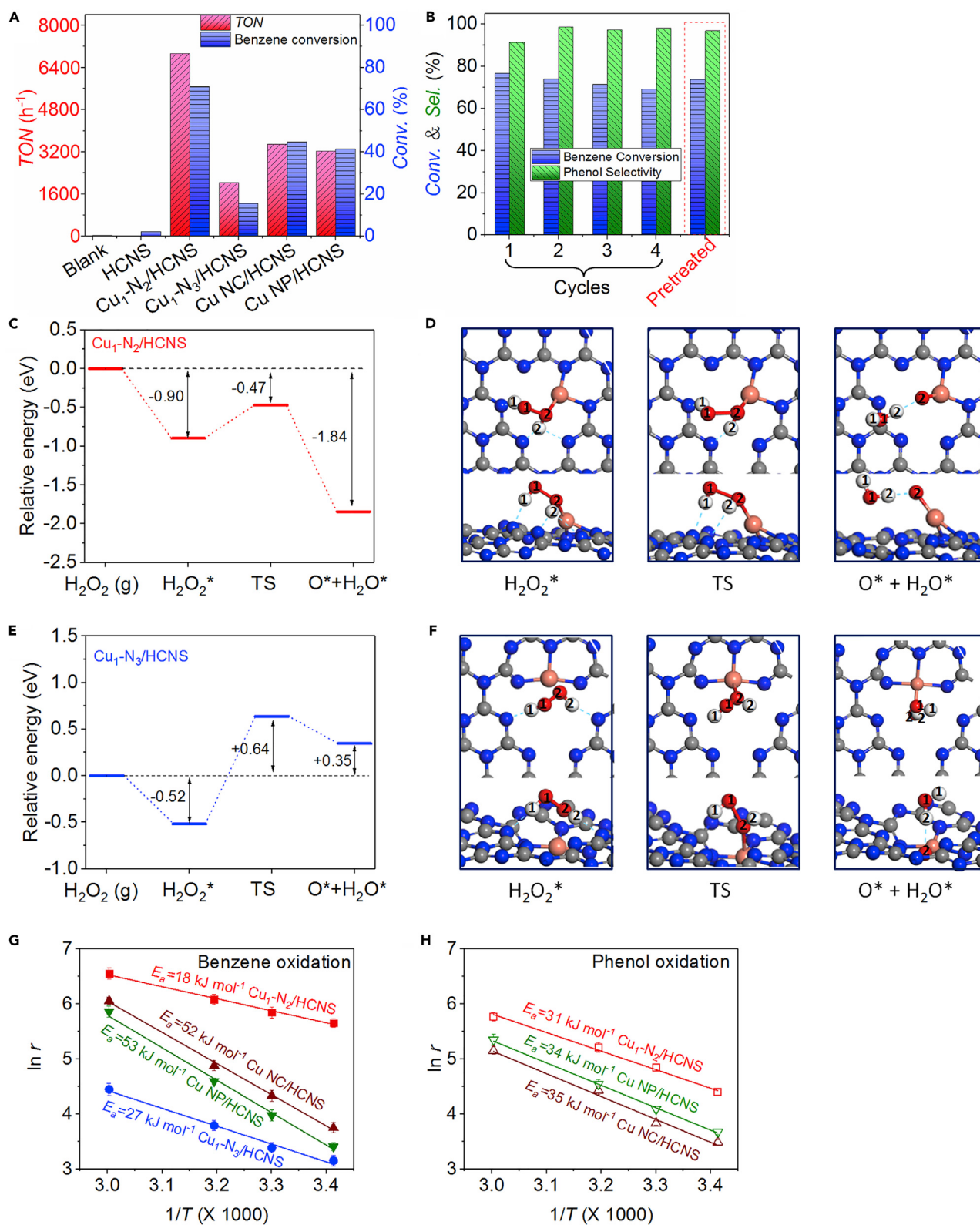


Figure 3. Catalytic Evaluation Results

(A) Catalytic activity for benzene hydroxylation to phenol over various catalysts. Reaction conditions: 0.013 mol% active copper, molar ratio of H_2O_2 to substrate is 10:1, 0.5 mL of benzene, 6 mL of CH_3CN , 60°C , 12 h for blank/HCNS, 2.5 h for the others.

(B) Recyclability of single-atom $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst. Reaction conditions: 0.013 mol% active copper, molar ratio of H_2O_2 to substrate is 10:1, 0.5 mL of benzene, 6 mL of CH_3CN , 2.5 h.

(C–F) Reaction pathways and energy diagrams for H_2O_2 activation and dissociation over $\text{Cu}_1\text{-N}_2/\text{HCNS}$ (C and D) and $\text{Cu}_1\text{-N}_3/\text{HCNS}$ catalysts (E and F). The values denote the relative energies referenced to the H_2O_2 molecule in gas phase together with the bare catalyst (gray, C; blue, N; orange, Cu; red, O; white, H).

(G and H) Arrhenius plot of diverse catalysts for benzene oxidation (G) and phenol oxidation (H), respectively. The “r” for c,d is reaction rate. Reaction conditions: 20 mg of catalyst, 0.20 mL of benzene/phenol, 3.0 mL of H_2O_2 (30 wt%), 6 mL of CH_3CN , 1.5 h.

$\text{Cu}_1\text{-N}_3/\text{HCNS}$ (Zhang et al., 2018a, 2018b) were chosen as benchmark under the same reaction conditions. The results show that only trace benzene is converted without catalyst (Blank) or over bare HCNS support. Like our previously reported $\text{Cu}_1\text{-N}_3/\text{HCNS}$ (Zhang et al., 2018a, 2018b), the developed single atomic $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst exhibits much higher selectivity and stability than Cu nanoparticles and nanoclusters for benzene hydroxylation to phenol. More interestingly, $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst exhibits 3.4 times TON (6,935) of $\text{Cu}_1\text{-N}_3/\text{HCNS}$ (2,034) under the same reaction conditions. From Table S4, under the same reaction conditions, 70.9% of benzene conversion with 91.3% of phenol selectivity over $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst can be achieved, whereas only 15.6% of conversion over $\text{Cu}_1\text{-N}_3/\text{HCNS}$ can be obtained, although it shows 99.3% of slightly higher selectivity. In fact, the more than 99.9% of selectivity is also obtained in the absence of catalyst or over the bare HCNS support. Furthermore, the developed $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst also shows much superior catalytic performance to the previously reported single-atom catalysts (Table S4), owing to the atomically dispersed Cu- N_2 moieties and the promoted accessibility of single Cu active sites by the porous hollow structure. Beyond the remarkable catalytic performance, the $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst also shows high recycling stability and reusability. Figure 3B displays no obvious decrease in benzene conversion over $\text{Cu}_1\text{-N}_2/\text{HCNS}$ after four cycles.

It has been revealed that the reaction parameters, such as molar ratio of H_2O_2 to benzene, reaction temperature, and type of catalyst, may affect the performance of liquid phase benzene oxidation over heterogeneous catalysts with H_2O_2 as oxidant (Evtushok et al., 2018; Acharyya et al., 2014). Data in Table S4 (Entry 3 and 12) demonstrate that the reaction temperature has an effect on the catalytic activity and selectivity of benzene oxidation over $\text{Cu}_1\text{-N}_2/\text{HCNS}$. When the reaction is carried out at 25°C , higher benzene TON compared with references is obtained, yet the phenol selectivity shows a disadvantage (see Table S4, Entry 12, 13, and 14). Surprisingly, when the reaction is carried out at 60°C (see Table S4, Entry 3), improved phenol selectivity with enhanced catalytic activity is obtained. The above-mentioned results indicate that a higher reaction temperature (60°C) may be beneficial for the improving of phenol selectivity over $\text{Cu}_1\text{-N}_2/\text{HCNS}$. This phenomenon is different from the reported results that high temperature leads to decreased phenol selectivity over single-atom Co-ISA/CNS catalyst (Evtushok et al., 2018).

Figure S8 gives the effect of molar ratio of H_2O_2 to benzene in liquid phase benzene oxidation over the $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst. The results clearly show that increasing the molar ratio of H_2O_2 to benzene (less than 10) leads to higher benzene conversion with invariable H_2O_2 utilization and phenol selectivity. However, when the molar ratio of H_2O_2 to benzene is further increased to 15, the benzene conversion displays no more observable increment, yet the H_2O_2 shows striking decrease.

From the aforementioned description, both the $\text{Cu}_1\text{-N}_2/\text{HCNS}$ developed in this work and the $\text{Cu}_1\text{-N}_3/\text{HCNS}$ reported in our previous work feature the single-atom catalyst, however, with different local atomic structures of Cu atoms. Different coordination environment of single-atom Cu catalyst results in quite distinct catalytic performance for liquid phase benzene oxidation (see Table S4, Entry 3 and 4). As previously reported (Ivanchikova et al., 2014; Su et al., 2017; Evtushok et al., 2018), the reaction pathway for benzene oxidation to phenol by H_2O_2 usually can be abstracted into two steps, including the first H_2O_2 decomposition for the formation of active oxygen species and the subsequent oxidation of benzene to phenol. The much different catalytic activity clearly displays that the benzene conversion is directly related to the H_2O_2 conversion since a similar H_2O_2 utilization efficiency over $\text{Cu}_1\text{-N}_2/\text{HCNS}$, $\text{Cu}_1\text{-N}_3/\text{HCNS}$, and Cu NC/HCNS catalysts can be observed (see Table S4, Entry 3, 4, and 5). This phenomenon implies that the different catalytic performance over diverse catalysts may derive from their discrepant abilities for the activation of H_2O_2 .

DFT Calculations for Reaction Mechanism

To compare the activity of $\text{Cu}_1\text{-N}_2/\text{HCNS}$ and $\text{Cu}_1\text{-N}_3/\text{HCNS}$ catalysts toward H_2O_2 adsorption and activation, DFT calculations were performed to identify intermediates and reaction pathways. The minimum energy pathways for H_2O_2 adsorption and dissociation on the Cu-N_2 and Cu-N_3 sites are illustrated in Figures 3C–3F, respectively, with all optimized structures included. On the $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst, the H_2O_2 oxidant is initially adsorbed by the active Cu site with the O–Cu distance of 1.90 Å. In the meantime, multiple hydrogen bonds are formed between the H atoms of H_2O_2 and N atoms of the catalyst, resulting in an activation of the O–O bond to 1.51 Å from 1.48 Å in gas phase. The binding energy of H_2O_2 is calculated to be -0.89 eV on the Cu-N_2 site. The activated H_2O_2^* can be easily transformed into the active O^* species by releasing a water molecule, with an energy barrier of only 0.42 eV and a reaction energy exothermic by -0.95 eV. As shown in the transition state configuration (see Figures 3C and 3D), the O–O bond length elongates to 1.68 Å from 1.51 Å, whereas the $\text{O}_1\text{-H}_2$ distance contracts to 1.75 Å from 2.00 Å in the adsorbed state, indicating that the O–O bond cleavage and O–H bond formation tend to occur concurrently in the H_2O_2 dissociation step. The Cu site still coordinates to the O_2 atom strongly, with a bond length of 1.82 Å in the transient state (TS). In the dissociated state, a H_2O molecule is formed, which is H-bonded to the active O^* species with the $\text{H}_2\text{-O}_2$ distance of 1.60 Å. Then, the formed active O^* species over the Cu-N_2 site is ready to react with benzene to form phenol.

On the $\text{Cu}_1\text{-N}_3/\text{HCNS}$ catalyst (see Figures 3E and 3F), the H_2O_2 molecule is still adsorbed over the Cu site, but the Cu–O interaction is weaker than that adsorption on the Cu-N_2 site, as evidenced by the longer distance of Cu– O_2 (2.58 Å) and the weaker binding energy of H_2O_2 (-0.52 eV, see Figure 3F). Although hydrogen bonds are formed between the H atoms of H_2O_2 and N atoms of the catalyst, we did not observe obvious activation of H_2O_2 upon adsorption on the Cu-N_3 site owing to the weak interaction with Cu, and the O–O bond length does not change compared with that in gas phase molecule. In the formation of active O^* species, Cu interaction with the O_2 atom is still weak in the transition state, with the Cu– O_2 bond length of 2.20 Å. This bond length is 0.38 Å longer than that in the transition state generated over the Cu-N_2 site, indicating an unstable transition state for active O^* formation over the Cu-N_3 site. Although the elementary pathways for H_2O_2 adsorption and dissociation are similar over $\text{Cu}_1\text{-N}_2/\text{HCNS}$ and $\text{Cu}_1\text{-N}_3/\text{HCNS}$ catalysts, the energy barrier of H_2O_2^* dissociation to O^* is up to 1.16 eV on the Cu-N_3 site, with an unfavorable reaction energy of 0.86 eV.

Comparing the energy pathways for H_2O_2 adsorption and dissociation on the two single-atom catalysts, clearly, the $\text{Cu}_1\text{-N}_2/\text{HCNS}$ is catalytically more active for both H_2O_2 activation and active O^* species formation, which would be a superior candidate for benzene oxidation than the $\text{Cu}_1\text{-N}_3/\text{HCNS}$ catalyst.

To supplement the DFT results, the comparative trials were rationally designed and carried out (see Figure S9). The excess benzene versus H_2O_2 was used to ensure that the *in situ* formed active oxygen from H_2O_2 is rapidly consumed. The results indicate that $\text{Cu}_1\text{-N}_2/\text{HCNS}$ shows a higher H_2O_2 activation rate with higher benzene conversion than $\text{Cu}_1\text{-N}_3/\text{HCNS}$ catalyst, firmly demonstrating that the much higher activity of $\text{Cu}_1\text{-N}_2/\text{HCNS}$ for selective oxidation of benzene compared with $\text{Cu}_1\text{-N}_3/\text{HCNS}$ catalyst may originate from its higher H_2O_2 activation ability.

Kinetic Studies of Benzene Oxidation

To get further experimental insight into the much superior catalytic performance of the developed single-atom $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst, kinetic studies of benzene oxidation were carried out in a kinetic controlled regime. From Figures 3G and S10 and Table S5, the two single-atom catalysts exhibit a lower apparent activation barrier (E_a) than that of supported nanocluster (Cu NC/HCNS) and nanoparticle (Cu NP/HCNS) catalysts for the benzene oxidation reaction. Moreover, the single atomic $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst demonstrates much lower E_a and much higher pre-exponential factor (A) concerning benzene oxidation than $\text{Cu}_1\text{-N}_3/\text{HCNS}$, originating from the different properties of Cu-N_2 catalytic sites and Cu-N_3 moieties. As a consequence, the $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst displays much higher TON for benzene selective oxidation to phenol in comparison with other catalysts (see Figure 3A and Table S4).

From the reaction results for selective oxidation of benzene shown in Table S4, the developed single atomic $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst exhibits a much higher selectivity toward phenol than Cu NC/HCNS and

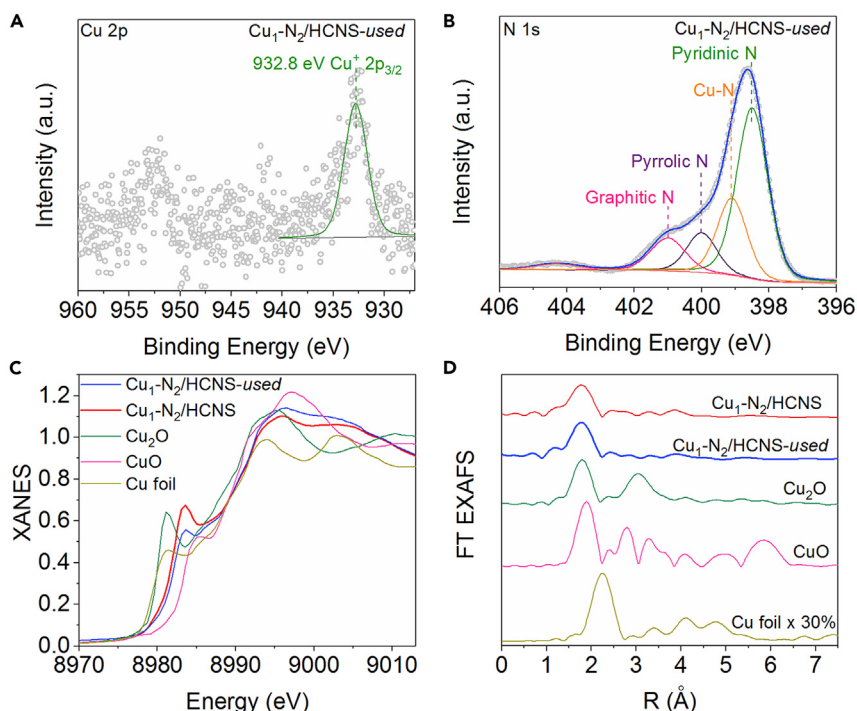


Figure 4. X-Ray Spectroscopy Analyses of the Used Single-Atom Catalyst

(A) Cu 2p XPS spectrum of $\text{Cu}_1\text{-N}_2/\text{HCNS-used}$.

(B) N 1s XPS spectrum of $\text{Cu}_1\text{-N}_2/\text{HCNS-used}$.

(C) Normalized Cu K-edge XANES spectra of Cu foil, CuO, Cu_2O , and $\text{Cu}_1\text{-N}_2/\text{HCNS-used}$.

(D) The k^3 -weighted Fourier transform spectra from Cu K-edge EXAFS.

Cu NP/HCNS catalysts. From our previous finding (Zhang et al., 2018a, 2018b), quinone confirmed by mass spectrometry, as the detected by-product, possibly results from the deep oxidation of as-formed phenol over $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst. Therefore, kinetic studies of phenol oxidation over $\text{Cu}_1\text{-N}_2/\text{HCNS}$, Cu NC/HCNS, and Cu NP/HCNS catalysts were carried out to explore the origin of the higher selectivity of $\text{Cu}_1\text{-N}_2/\text{HCNS}$ than the other two. As shown in Figures 3H and S11, and Table S5, $\text{Cu}_1\text{-N}_2/\text{HCNS}$ exhibits a slightly lower A than Cu NC/HCNS and Cu NP/HCNS for phenol oxidation to quinone, indicating the unfavorable for phenol oxidation. Furthermore, as shown as earlier, $\text{Cu}_1\text{-N}_2/\text{HCNS}$ exhibits much lower E_a with much higher A for benzene oxidation than Cu NC/HCNS and Cu NP/HCNS (Table S5). As a consequence, $\text{Cu}_1\text{-N}_2/\text{HCNS}$ exhibits much higher selectivity for hydroxylation of benzene to phenol than Cu NC/HCNS and Cu NP/HCNS catalysts.

In other words, the extremely higher activity of $\text{Cu}_1\text{-N}_2/\text{HCNS}$ compared with $\text{Cu}_1\text{-N}_3/\text{HCNS}$ originates from its much higher H_2O_2 activation and lower E_a with much higher A for benzene oxidation. The much higher phenol selectivity of $\text{Cu}_1\text{-N}_2/\text{HCNS}$ compared with Cu NC/HCNS and Cu NP/HCNS derives from the much lower E_a with much higher A for benzene oxidation but the comparable E_a with slightly lower A for phenol oxidation to quinone.

The developed $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst in this work shows high recycling stability and reusability. ICP and XPS results indicate the Cu content of the used catalyst is similar to that of the fresh catalyst (Table S6), demonstrating that the single Cu atoms are firmly anchored on HCNS owing to the strong coordination of Cu-N bond (see Figures 4A and 4B). More interestingly, the phenol selectivity increases from 91.5% to 97%–99% from the second cycle (see Figure 3B). The XANES profile of $\text{Cu}_1\text{-N}_2/\text{HCNS-used}$ (see Figures 4C, 4D, and S12) determines a slight increase of oxidation state of Cu from +1.5 to +1.7 (see Table S3), correlating to the larger CN value of Cu-O from 0.9 to 1.4 via EXAFS fit, indicating the possible oxidation of Cu by H_2O_2 during the reaction process thus inducing the variation of local atomic structure of single-atom Cu. The increased phenol selectivity may result from the variation of the local atomic structure of

single Cu atom. To verify this hypothesis, the controlled experiment was performed. Figure 3B shows that the phenol selectivity increases to 97% over the H₂O₂ pretreated Cu₁-N₂/HCNS, firmly proving our aforementioned hypothesis. The developed Cu₁-N₂/HCNS catalyst shows outstanding catalytic performance for hydroxylation of benzene to phenol, and more than 70% of benzene conversion with close to 99% of phenol selectivity has been obtained.

Conclusions

In summary, we present a facile reduction deposition-acid leaching strategy for preparing the single atomic Cu₁-N₂/HCNS catalyst. Owing to the unique local atomic structure of Cu atom center, the single-atom Cu-N₂ catalytic sites are far superior to Cu-N₃ sites with the former showing 3.4 times higher TON for benzene hydroxylation to phenol compared with the latter under the same reaction conditions. Moreover, Cu₁-N₂/HCNS catalyst demonstrates much higher selectivity (close to 99%) and stability than Cu nanoparticles and nanoclusters. The unique Cu-N₂ sites anchored on the g-C₃N₄ surface are responsible for the outstanding catalytic properties concerning activity, selectivity, and stability for benzene hydroxylation to phenol, and the unique Cu-N₂ is extremely more active than Cu-N₃ owing to its much lower energy barrier regarding H₂O₂ activation owing to the unique coordination state of local atomic structure, confirmed by the results from experiments and DFT calculations. This work not only generates an efficient benzene hydroxylation catalyst for phenol production, but also presents a facile and efficient method for modulating coordination environment of single metallic atoms to design excellent catalysts.

Limitations of the Study

In this paper, we have proved that single-atom catalyst with Cu-N₂ sites shows extremely high activity than Cu-N₃ sites for benzene hydroxylation with H₂O₂ to phenol. However, our current evaluation system needs a large amount of H₂O₂ for a high benzene conversion, which results in a relatively low utilization of H₂O₂ because of its invalid decomposition.

METHODS

All methods can be found in the accompanying [Transparent Methods supplemental file](#).

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at <https://doi.org/10.1016/j.isci.2019.11.010>.

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AUTHOR CONTRIBUTIONS

T.Z. conceived and performed the experiments, collected and analyzed data, and wrote the paper. X.N. conducted the density functional theory calculation, analysis, and also wrote this section. W.Y. participated in the synthesis of materials. X.G. participated in the data analysis and discussions. C.S. participated in the data analysis and discussions and also revised the paper. R.S. performed XAS measurement and participated in the XAS data analysis and wrote this section. Y.L. conducted the HAADF-STEM studies. Z.Z. conceived the idea, supervised the project work, and led the data analysis and discussion, and prepared and finalized the paper. All the authors commented on the manuscript and have given approval to the final version of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

Single Atomic Cu-N₂ Catalytic Sites for Highly Active and Selective Hydroxylation of Benzene to Phenol

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Supporting Information

Supplemental Data Items

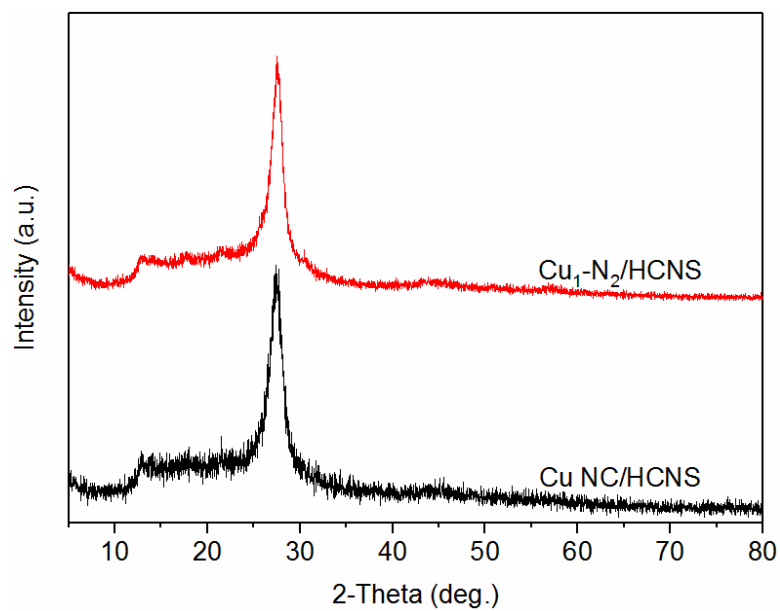


Figure S1. The XRD Patterns of Cu NC/HCNS and Cu₁-N₂/HCNS, related to Figure 1.

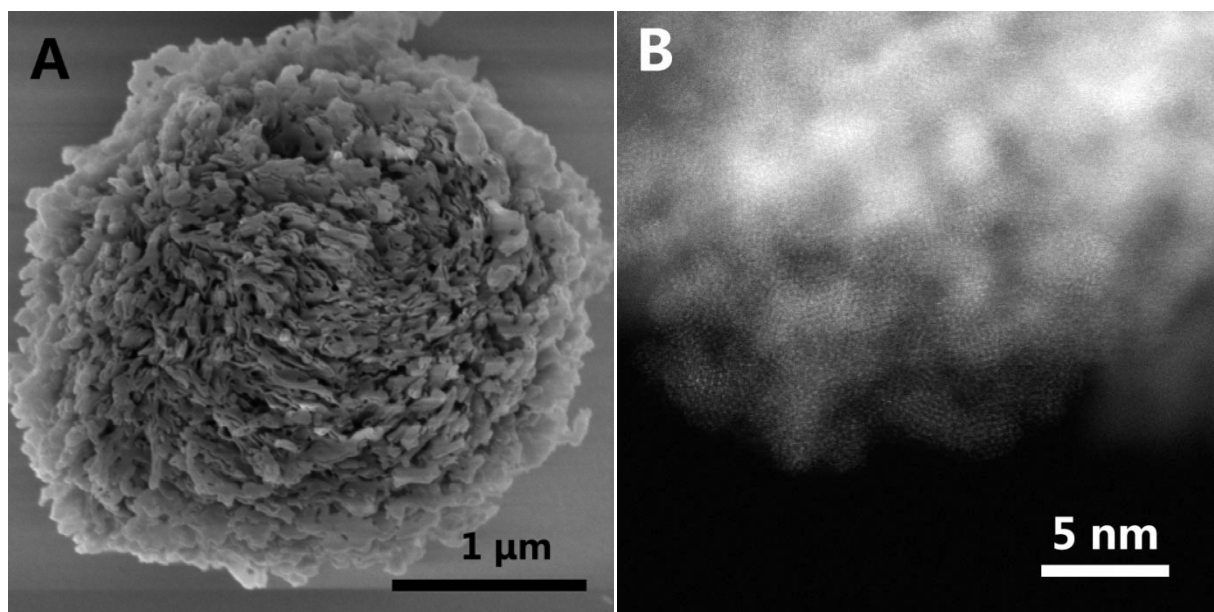


Figure S2. (A) SEM Image of Single-atom $\text{Cu}_1\text{-N}_2/\text{HCNS}$ Catalyst and (B) HAADF-STEM image of Cu NC/HCNS, related to Figure 1.

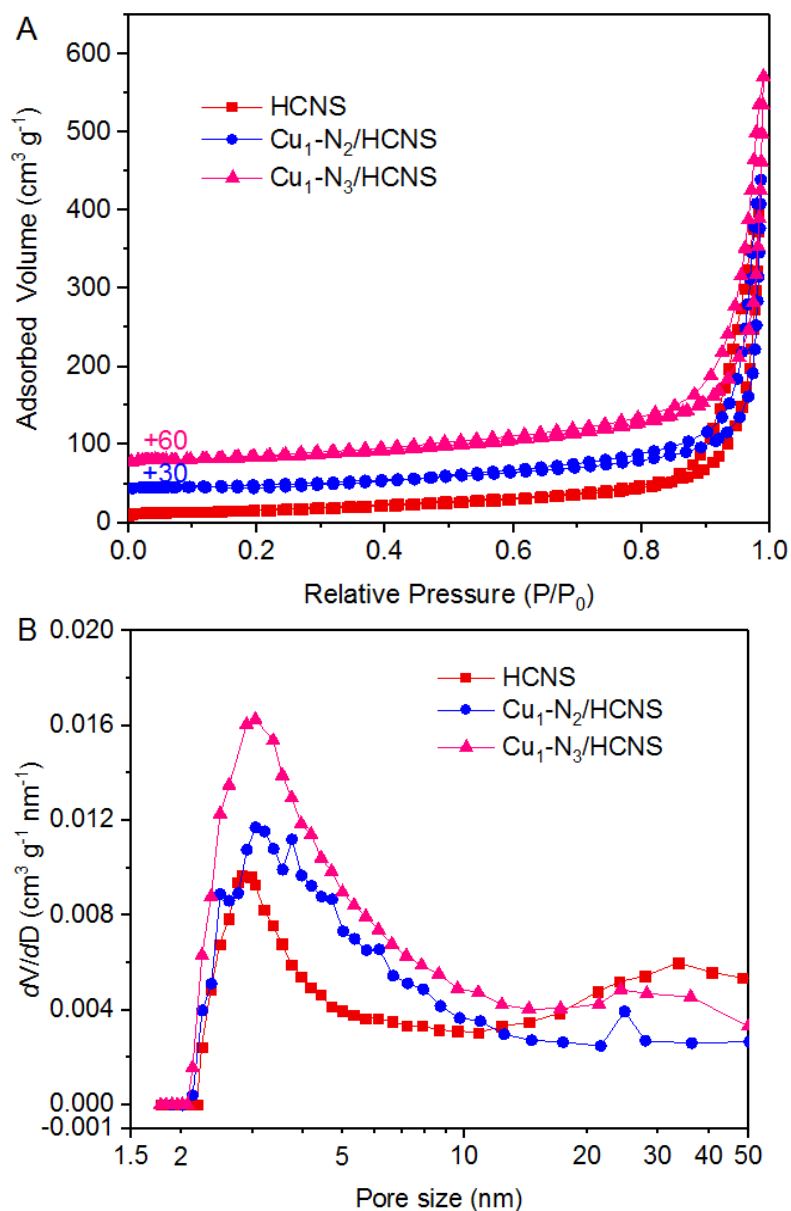


Figure S3. Nitrogen Physisorption Analysis of Single-atom $\text{Cu}_1\text{-N}_2/\text{HCNS}$ Catalyst, $\text{Cu}_1\text{-N}_3/\text{HCNS}$ Catalyst and HCNS Support, related to Figure 1.

(A) Isotherms curves

(B) Pore size distribution curves

Table S1. Textural Properties of Single-atom Cu₁-N₂/HCNS Catalyst and HCNS Support, related to Figure 1.

Entry	Sample	S _{BET} (m ² ·g ⁻¹)	V _{BJH} (cm ³ ·g ⁻¹)	V _{Total} (cm ³ ·g ⁻¹)
1	HCNS	57	0.64	0.64
2	Cu ₁ -N ₂ /HCNS	65	0.67	0.67
3	Cu ₁ -N ₃ /HCNS	84	0.82	0.82

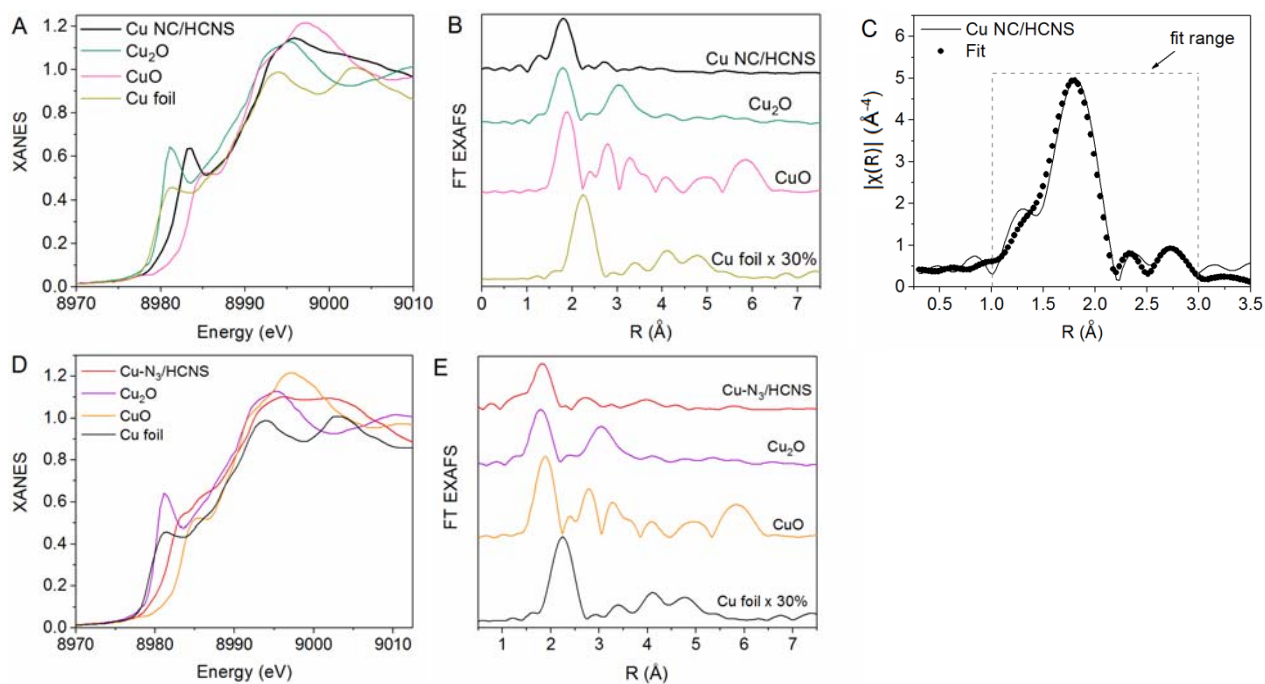


Figure S4. XAFS Analysis, related to Figure 1.

(A) Normalized Cu K-edge XANES spectra of Cu foil, CuO, Cu₂O and Cu NC/HCNS.

(B) The k^3 -weighted Fourier transform spectra from Cu K-edge EXAFS.

(C) The corresponding EXAFS fitting curve of Cu NC/HCNS.

(D) Normalized Cu K-edge XANES spectra of Cu foil, CuO, Cu₂O and Cu₁-N₃/HCNS.

(E) The k^3 -weighted Fourier transform spectra from Cu K-edge EXAFS of Cu foil, CuO, Cu₂O and Cu₁-N₃/HCNS.

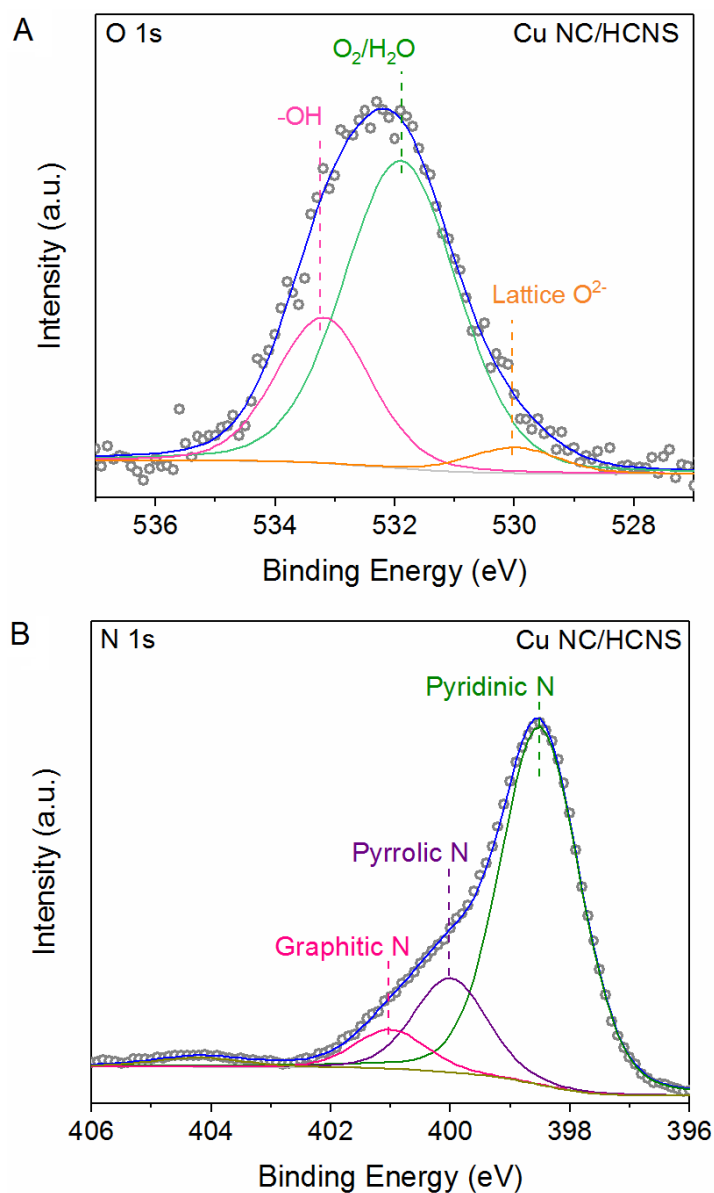


Figure S5. XPS analysis of Cu NC/HCNS catalyst, related to Figure 1.

(A) O 1s XPS spectrum.

(B) N 1s XPS spectrum.

Table S2. EXAFS fitting data for Cu NC/HCNS catalyst, related to Figure 1.

Sample	Cu-N (O)		Cu-Cu		σ^2 (Å ²) ^c	ΔE_0^d (eV)	Valence
	R (Å) ^a	CN ^b	R (Å) ^a	CN ^b			
Cu NC/HCNS	1.92±0.01(O)	2.9±0.3(O)	2.87±0.04	0.4±0.2	0.007±0.001(N,O) 0.010±0.006(Cu)	7.6±0.9	+1.6
Cu ₁ -N ₃ /HCNS ^e	1.96±0.01(N)	3.3±0.3(N)	-	-	0.007±0.001(N)	10.8±1.3	+1.6

^aBond distance;

^bCoordination number;

^cDebye-Waller factor;

^dInner potential correction.

^eCited from Ref. ([Zhang et al., 2018](#))

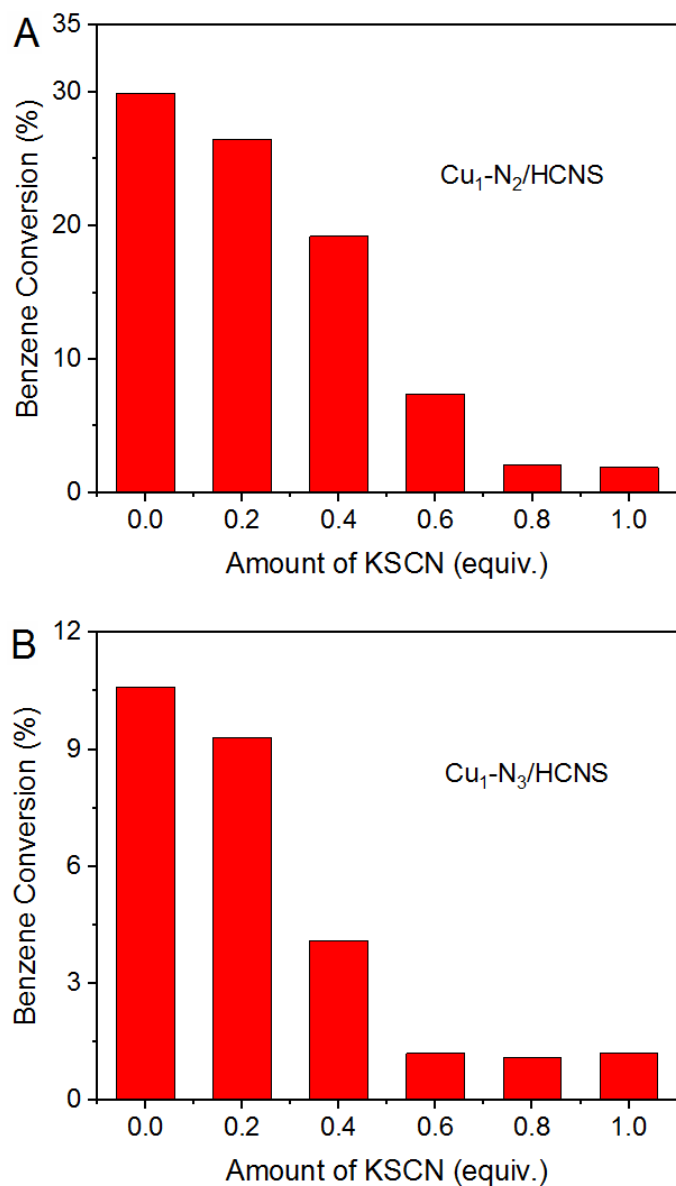


Figure S6. KSCN titration for determining the amount of active Cu sites, related to Figure 1.

Before the reaction carried out, single-atom catalyst was treated with certain amount of KSCN in water solution for 2 h. The amount of KSCN was calculated according to the total Cu content from ICP result. The following reaction was performed under following conditions: benzene (0.4 mL), H_2O_2 (6 mL) and acetonitrile (3 mL), 60 °C for 0.5 h.

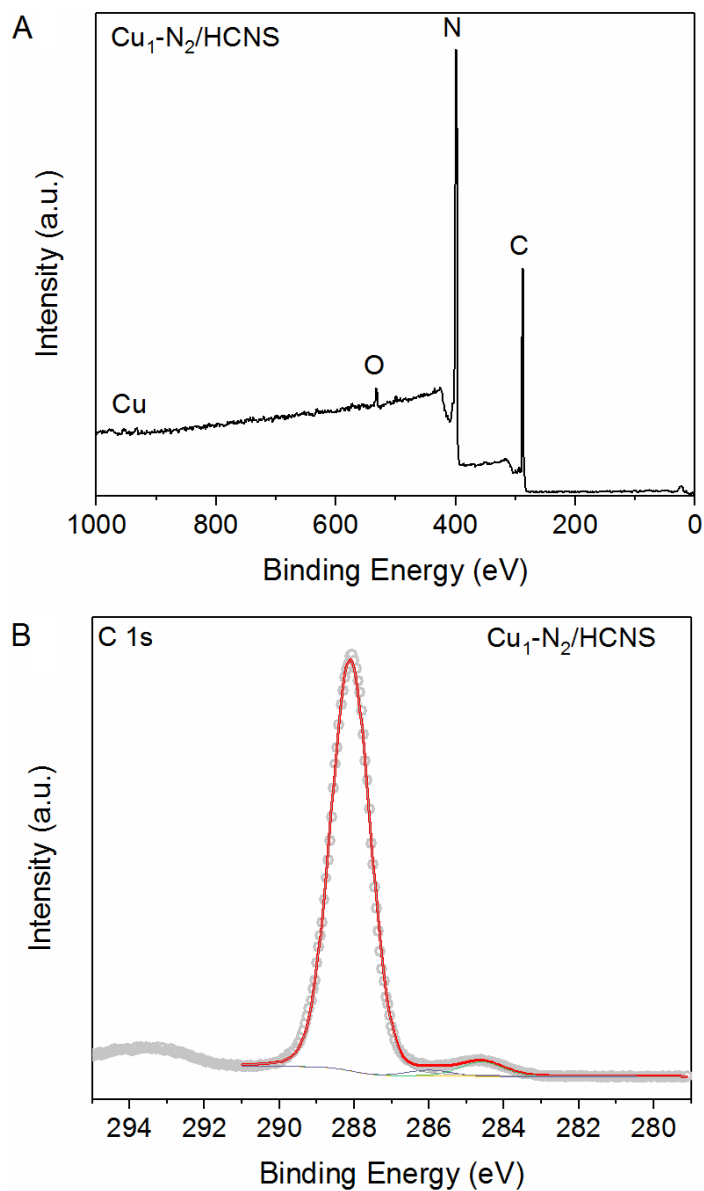


Figure S7. XPS analysis of $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst, related to Figure 2.

(A) The survey XPS spectrum.

(B) The C 1s XPS spectrum.

Table S3. EXAFS fitting data for the fresh and used Cu₁-N₂/HCNS single-atom catalyst, related to Figure 2 and Figure 4.

Sample	Cu-N/O		Cu-Cu		σ^2 (Å ²) ^c	ΔE_0 ^d (eV)	Valence
	R (Å) ^a	CN ^b	R (Å) ^a	CN ^b			
Cu ₁ -N ₂ /HCNS	1.92±0.03(N)	2.0(N)	-	-	0.007±0.001(N,O)	7.6±0.9	+1.5
	1.96±0.05(O)	0.9±0.4(O)					
Cu ₁ -N ₂ /HCNS-used ^e	1.94±0.07(N)	2.0(N)	-	-			+1.7
	1.97±0.07(O)	1.4±1.0(O)					

^aBond distance.^bCoordination number.^cDebye-Waller factor.^dInner potential correction.^eThe sample was recovered after one reaction cycle.

Table S4. Catalytic Performance of Various Catalysts for Direct Hydroxylation of Benzene to Phenol, related to Figure 3.

Entry	Sample	Temp. (°C)	Time (h)	Conv. (%)		TON of Benzen	Sel. (%)			Utilization of H ₂ O ₂	Ref.
				Benzene	H ₂ O ₂		Phenol	<i>p</i> -benzoquinone	others		
1 ^a	Blank	60	12	1.5	-	-	>99.9	-	-	-	
2 ^a	HCNS	60	12	5.2	-	-	>99.9	-	-	-	
3 ^a	Cu ₁ -N ₂ /HCNS	60	2.5	70.9	47.3	6935	91.1	8.9	<0.1	15	This work
4 ^a	Cu ₁ -N ₃ /HCNS	60	2.5	15.6	11.6	2034	99.3	0.7	<0.1	14	
5 ^a	Cu NC/HCNS	60	2.5	44.7	25.5	3489	73.0	27.0	<0.1	16	
6 ^a	Cu NP/HCNS	60	2.5	41.4	-	3231	70.9	29.1	<0.1	-	
7 ^a	Cu ₁ -N ₂ /HCNS	60	12	76.8	-	-	91.5	8.5	<0.1	-	This work
8 ^b	Cu ₁ -N ₂ /HCNS	60	3.5	89.3	-	2783	90.5	9.5	<0.1	-	This work
9 ^b	Co-ISA/CNS	60	24	82.0	-	<722	86.0	-	-	-	Zhu et al., 2018
10	[Ni(tepa)] ²⁺	60	216	7.5	-	749	99.0	-	-	-	Morimoto, 2015
11 ^a	SA-Fe/CN	60	24	45	-	786	94.0	-	-	-	Zhang et al., 2017
12 ^b	Cu ₁ -N ₂ /HCNS	25	24	81.2	-	2531	86.6	13.4	<0.1	-	This work
13 ^b	Co-ISA/CNS	25	24	53.0	-	<511	93.0	-	-	-	Zhu et al., 2018
14 ^b	FeN ₄ /GN-2.7	25	24	23.4	-	44	80.0	-	-	-	Zhang et al., 2017

^aReaction conditions: 0.013 mol% active copper, molar ratio of H₂O₂ to substrate is 10:1, 0.5 mL of benzene, 6 mL of CH₃CN.

^bReaction conditions: 50.0 mg catalyst, 0.4 mL benzene, 6 mL H₂O₂ (30 wt%), 3 mL CH₃CN.

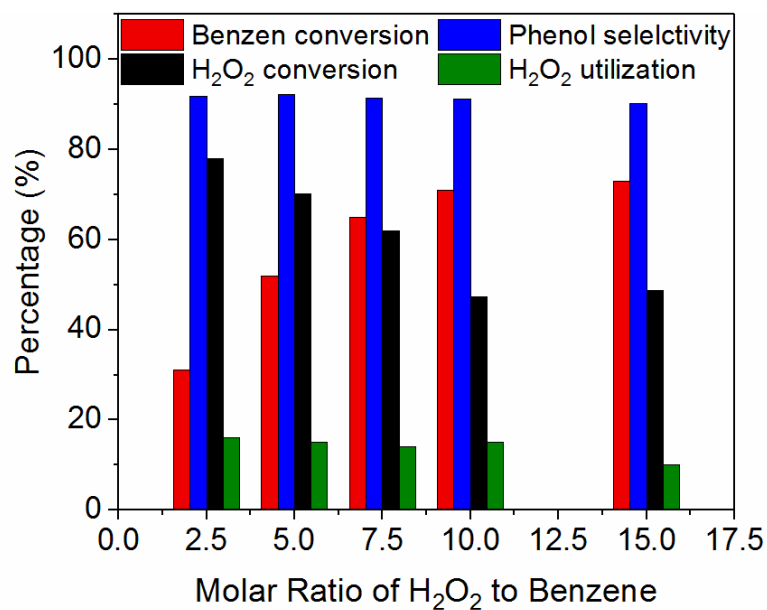


Figure S8. Effect of the Molar Ratio of H₂O₂ to Benzene in Benzene Oxidation over Cu₁-N₂/HCNS Catalysyt, related to Figure 3.

Reaction conditions: 20 mg catalyst, 0.5 mL benzene, 6 mL CH₃CN, and different amount of H₂O₂ (30%) at 60 °C for 2.5 h.

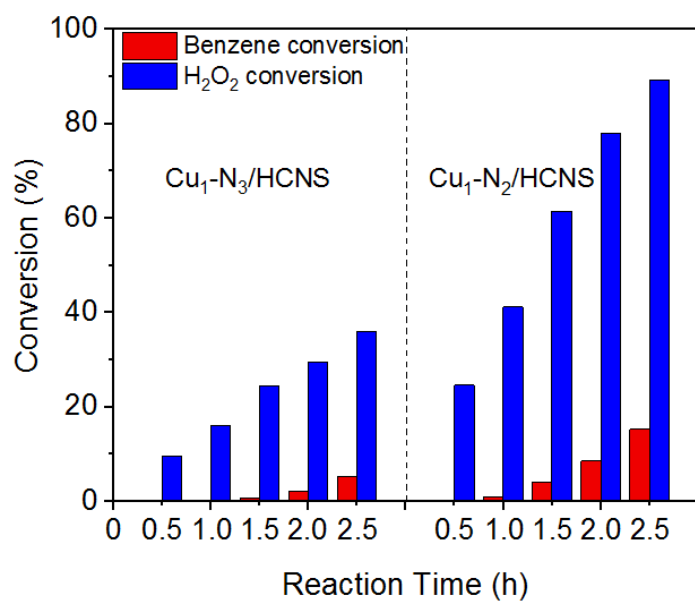


Figure S9. Comparative Trials for H₂O₂ Decomposition in Benzene Oxidation over Cu₁-N₂/HCNS Catalyst, related to Figure 3.

Reaction conditions: 0.0065 mol% active copper, 1.0 mL benzene (11 mmol), 0.52 mL H₂O₂ (30%) (5.5 mmol), and 6 mL CH₃CN at 60 °C.

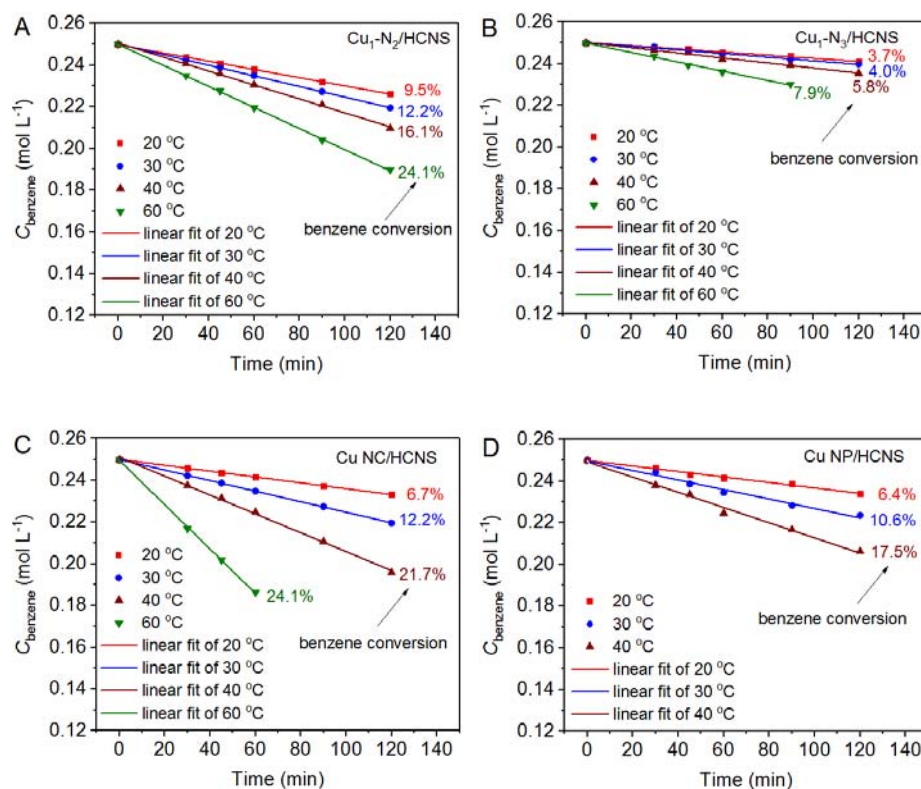


Figure S10. The Kinetic Data Concerning Variation of Benzene Concentration as a Function of Reaction Time at Different Temperatures in the Kinetic Controlled Regime, related to Figure 3.

Reaction conditions: 20 mg of Cat., 0.20 mL of benzene, 3.0 mL of H_2O_2 (30 wt%), 6 mL of CH_3CN . The data of $\text{Cu}_1\text{-N}_3/\text{HCNS}$ and $\text{Cu NP}/\text{HCNS}$ is cited from Ref. ([Zhang et al., 2018](#)).

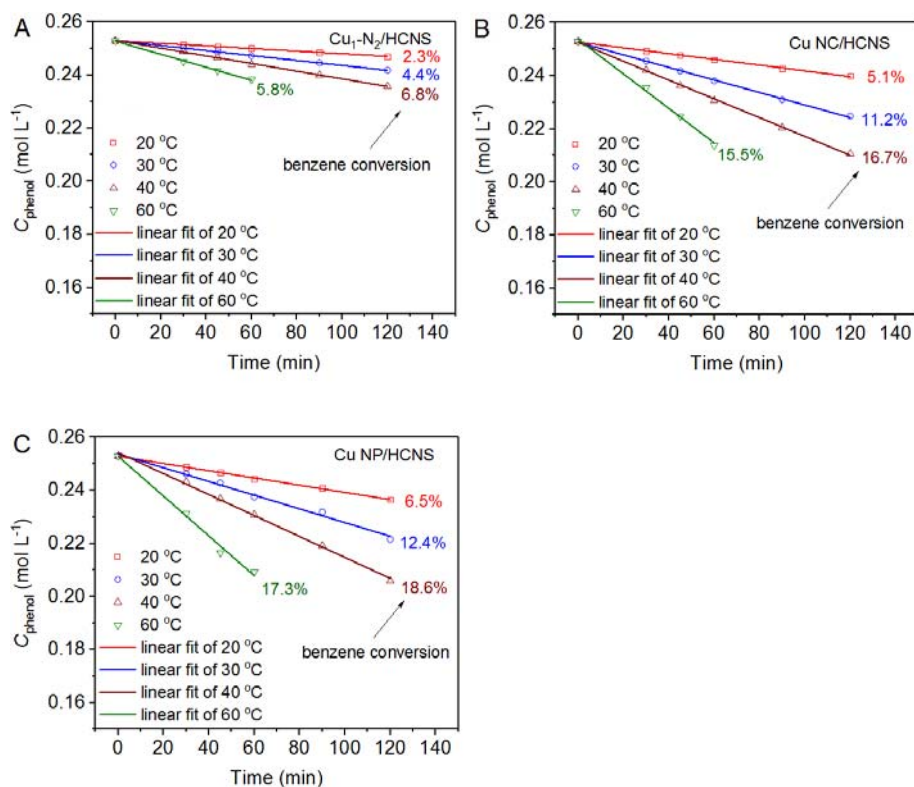


Figure S11. The Kinetic Data Concerning Variation of Phenol Concentration as a Function of Reaction Time at Different Temperatures in the Kinetic Controlled Regime, related to Figure 3.

Reaction conditions: 20 mg of Cat., 0.20 mL of phenol, 3.0 mL of H₂O₂ (30 wt%), 6 mL of CH₃CN. The data of Cu NP/HCNS is cited from Ref. ([Zhang et al., 2018](#)).

Table S5. The Comparison of Kinetic Parameters of Benzene Oxidation and Phenol Oxidation over Various Catalysts, related to Figure 3.

Reaction	E_a (kJ mol ⁻¹)				$A_{\text{Cu1-N3/HCNS/}}$ $A_{\text{Cu1-N2/HCNS}}$	$A_{\text{Cu NC/HCNS/}}$ $A_{\text{Cu1-N2/HCNS}}$	$A_{\text{Cu NP/HCNS/}}$ $A_{\text{Cu1-N2/HCNS}}$
	Cu ₁ -N ₂ /HCNS	Cu ₁ -N ₃ /HCNS ^a	Cu NC/HCNS	Cu NP/HCNS ^a			
Benzene oxidation	18	27	52	53	1/8.0	1/1.4	1/1.2
Phenol oxidation	31	40	35	34	-	1.2/1	1.1/1

^aFrom Ref. ([Zhang et al., 2018](#)).

Table S6. Surface Component of Cu₁-N₂/HCNS Before and After Reaction^a, related to Figure 4.

Sample	C ^b (At. %)	N ^b (At. %)	O ^b (At. %)	Cu ^b (At. %)	Cu ^c (wt %)
Cu ₁ -N ₂ /HCNS	41.84	56.13	1.78	0.25	0.23
Cu ₁ -N ₂ /HCNS-used	45.72 ^d	49.10 ^d	4.93 ^d	0.25 ^d	0.21 ^e

^aReaction conditions: 20 mg of Cat., 6 mL of CH₃CN, 5.2 mL of H₂O₂, 0.5 mL of benzene, 60 °C for 12 h.

^bXPS results.

^cICP-AES results.

^dThe solid catalyst was recovered after 1 cycle.

^eThe solid catalyst was recovered after 4 cycles.

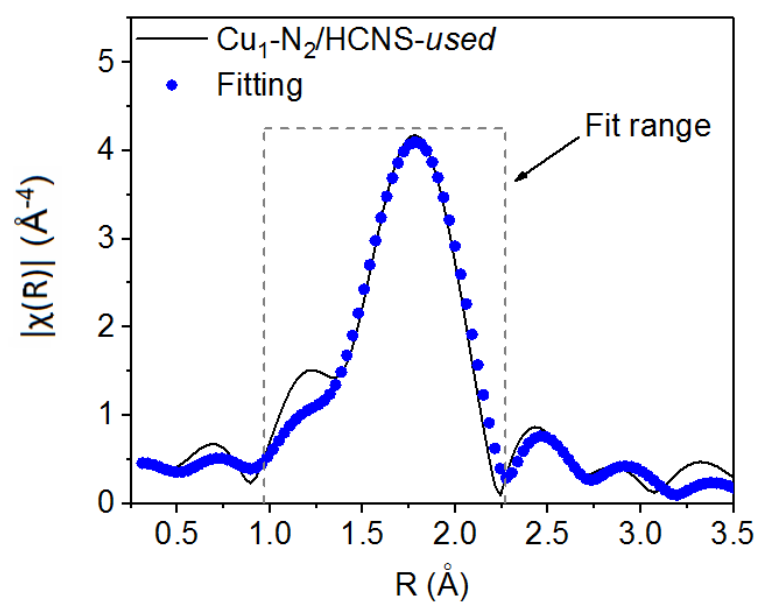


Figure S12. The Corresponding EXAFS Fitting Curve of $Cu_1-N_2/HCNS-used$ Catalyst, related to Figure 4.

Transparent Methods

Chemicals

Melamine, cyanuric acid, copper nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), acetonitrile (CH_3CN), *n*-tetradecane and chloroform (CH_3Cl) were supplied by Tianjin Fuyu Fine Chemical Co., Ltd. Copper(II) acetate monohydrate ($\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$), dimethyl sulfoxide (DMSO) and H_2O_2 (30%) were purchased from Damao Chemical Reagent Factory. Polyvinylpyrrolidone (PVP-K30) and potassium rhodanate (KSCN) were obtained from Sigma. Nitric acid (HNO_3 , 65~68 wt%), sodium hydroxide (NaOH) and sodium borohydride (NaBH_4) were supplied by Tianjin Guangfu Technology Development Co., Ltd. All the chemical reagents were analytical grade and directly used without further purification.

Preparation of Hollow Carbon Nitride Spheres (HCNS)

The hollow carbon nitride spheres (HCNS) was prepared corresponding to reference([Jun, 2013](#); [Jun, 2013](#)). Typically, 0.5 g of melamine and 0.51 g of cyanuric acid were ultrasonically dissolved in 20 mL and 10 mL of DMSO, respectively. After that, the two DMSO solutions were mixed together to obtain the white precipitates. As a consequence, the resulting solid was recovered by filtering and washing with ethanol. Finally, the HCNS was obtained by the drying at 50 °C with the subsequent calcination at 550 °C for 4 h with the heating rate under nitrogen atmosphere.

Preparation of $\text{Cu}_1\text{-N}_3/\text{HCNS}$ Catalyst

For comparison, the supported $\text{Cu}_1\text{-N}_3$ catalyst on HCNS was prepared according to our previous report.([Zhang et al., 2018](#)) Typically, the designed amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was firstly mixed with melamine in DMSO and magnetic stirring for 10 min, the DMSO dissolved cyanuric acid was added and keep stirring for 10 min. Solid sample was obtained by filtration and washed with water and ethanol. Dried solid was calcinated under N_2 atmosphere at 550 °C for 4 h. The final obtained solid catalyst was denoted as $\text{Cu}_1\text{-N}_3/\text{HCNS}$. The Cu content is 0.85 wt% determined by ICP-AES.

Preparation of Cu NP/HCNS Catalyst

For comparison, the supported Cu nanoparticle catalyst on HCNS was prepared by a modified adsorption method.([Nishimura, 2010](#)) Typically, a) 0.12 g of PVP-K30 was dissolved in 5 mL of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ aqueous solution (0.02 M) under N_2 atmosphere. b) 1 mL of reductant (1.2 mmol NaBH_4 and 1.0 mmol NaOH) was injected and the system was stirring for 12 h. c) 0.5 g of HCNS was added and kept stirring for 4 h. d) Solid sample was recovered by centrifugation and washed with water for 3 times, ethanol for 1 times, respectively. The solid catalyst was dried and denoted as Cu NP/HCNS. The Cu content is 0.85 wt% determined by ICP-AES.

Characterization of Catalysts

Low-magnification field emission scanning electron microscopy (FESEM) images were recorded by a FEI QUANTA 450 scanning electron microscopy. The transmission electron microscopy (TEM), high-resolution TEM, HAADF-STEM images were collected on a JEOL-ARM200F FETEM with 200kV of electron acceleration energy. X-ray photoelectron spectra (XPS) were recorded on an Al $\text{K}\alpha$ radiated Thermo VG ESCALAB250 instrument. The binding energy (BE) was calibrated by C 1s peak at 284.6 eV as the internal standard, and the deconvolution of spectra were carried out using the XPS PEAK 41 program with Gaussian function after subtracted by a Shirley background. Cu content was

determined by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). Nitrogen adsorption-desorption isotherms were recorded by 3H-2000PSI system of Beishide apparatus at 77 K. A degas process was performed at 140 °C for 6 h before the test. Brunauer-Emmett-Teller (BET) model was applied for the analysis of the porosity with the pore volume measured at $P/P_0 = 0.99$ point. The mesopore size distribution was calculated by BJH method from adsorption branch.

N₂O Titration Experiment

The content of surface active Cu atoms of Cu-NP/HCNS was determined by N₂O titration method on a Builder PCA-1200 apparatus equipped with a thermal conductor detector (TCD).[\(Zhang et al., 2018; Nishimura, 2010\)](#) Typically, a quartz “U” tube loaded with 100 mg sample of Cu-NP/HCNS was equipped and was firstly pretreated with Ar at 300 °C for 0.5 h. After the sample was reduced by 10 % H₂/Ar at 250 °C for 0.5 h, the tube was purged with Ar at 35 °C for 0.5 h. Subsequently, the sample was oxidized with N₂O for a period of time. When the TCD baseline stays steady, N₂O was replaced by Ar and the tube was purged for another 0.5 h. Later, the sample was reduced under 10 % H₂/Ar atmosphere at 200 °C for 0.5 h with a heating rate of 10 °C/min. The surface consumed H₂ was 3.4×10^{-3} mmol calculated through calibration, and the dispersity of Cu active sites was 26 %.

KSCN Titration Experiment

To determine the amount of exposed active Cu on the surface of the single-atom catalysts, KSCN titration method was applied. Typically, 50 mg single-atom catalyst was firstly loaded in a 50 mL flask. Then, a special equivalent of KSCN with 10 mL DI water was added. After magnetic stirring for 2 h, the solid catalyst was separated by centrifugation. Subsequently, the solid catalyst was transferred into the reaction system consist of benzene (0.4 mL), H₂O₂ (6 mL) and acetonitrile (3 mL). The following reaction was performed at 60 °C for 0.5 h.

XAFS Analysis

The X-ray absorption fine structure (XAFS) spectra at Cu K ($E_0 = 8979.0$ eV) edge was performed at BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) operated at 3.5 GeV under “top-up” mode with a constant current of 260 mA. The XAFS data were recorded under fluorescence mode with a Lytle-type ion chamber. The energy was calibrated accordingly to the absorption edge of pure Cu foil. Athena and Artemis codes were used to extract the data and fit the profiles. For the X-ray absorption near edge structure (XANES) part, the experimental absorption coefficients as function of energies $\mu(E)$ were processed by background subtraction and normalization procedures, and reported as “normalized absorption” with $E_0 = 8979.0$ eV for all the tested samples and Cu/Cu₂O/CuO standard. Based on the normalized XANES profiles, the molar fraction of Cu²⁺/Cu⁺/Cu⁰ can be determined by the linear combination fit [\(Kuld, 2014\)](#) with the help of various references (Cu foil for Cu⁰, Cu₂O for Cu⁺ and CuO for Cu²⁺). For the extended X-ray absorption fine structure (EXAFS) part, the Fourier transformed (FT) data in R space were analyzed by applying first-shell approximate model for Cu-N, Cu-O and Cu-Cu contributions. The passive electron factors, S_0^2 , were determined by fitting the experimental data on Cu foil and fixing the coordination number (CN) of Cu-Cu to be 12, and then fixed for further analysis of the measured samples. The parameters describing the electronic properties (e.g., correction to the photoelectron energy origin, E_0) and local structure environment including CN , bond distance (R) and Debye-Waller factor around the absorbing atoms were allowed to

vary during the fit process. The fitted ranges for k and R spaces were selected to be $k = 3\text{--}10 \text{ \AA}^{-1}$ ($\text{Cu}_1\text{-N}_2/\text{HCNS}$) or $3\text{--}12 \text{ \AA}^{-1}$ ($\text{Cu NC}/\text{HCNS}$) with $R = 1.0\text{--}3.0 \text{ \AA}$ (k^3 weighted).

Computational Methods

The Vienna *ab initio* simulation package (VASP) was applied for all spin-polarized DFT calculations, with the ion cores represented by the projector augmented wave (PAW) potentials (Blöchl, 1994; Kresse, 1996; Kresse, 1999). The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional (Kresse, 1999) was used to calculate the electronic exchange-correlation energy. A 400 eV of the cutoff energy was used for plane-wave basis set. Structure optimizations were conducted using a damped molecular dynamics method until the forces on all atoms were less than 0.02 eV/Å. Transition states were searched using the climbing image nudged elastic band (CI-NEB) method (Prdew, 1996; Henkelman, 2000), and each transition state was confirmed to have a single imaginary vibrational frequency along the reaction coordinate. A periodic monolayered $g\text{-C}_3\text{N}_4$ model in a 2×2 supercell was constructed and the optimized lattice parameters were recalculated to be $a = b = 14.32 \text{ \AA}$ and $c = 10.00 \text{ \AA}$. A $2 \times 2 \times 1$ k -point sampling within the Monkhorst-Pack scheme was employed for structural relaxations. The vacuum thickness was set to 10 Å to avoid interactions between repeating slabs. To compare the reactivity of benzene oxidation between the $\text{Cu}_1\text{-N}_2/\text{HCNS}$ and $\text{Cu}_1\text{-N}_3/\text{HCNS}$ catalyst, the C atom at different locations were separately replaced by a single Cu atom to model the Cu- N_2 and Cu- N_3 sites, as illustrated in Figure 2i and j. The binding energy of adsorbate was calculated by subtracting the energies of the isolated adsorbate in gas phase and the bare catalyst from the total energy of the adsorbed system.

Catalytic Performance Test

Selective oxidation of benzene to phenol was performed as the probe evaluation for catalytic performance test. Typically, a certain amount of catalyst (0.046 mg of active Cu atoms, 6 mL of CH_3CN , 0.5 mL of benzene and 5.2 mL of H_2O_2 (30 wt%) were mixed in a 50 mL round-bottom glass flask and sealed carefully. Then the reaction was carried out at 60 °C in a water bath kettle with magnetic stirring for a period of time. After the reaction was accomplished and the system cooled down to room temperature, products were extracted by dichloromethane, and *n*-tetradecane was injected as internal standard. The final products were analyzed by Fuli 9790II gas chromatograph equipped with a 30 m $\times$ 0.32 mm $\times$ 0.50 μm SE-54 capillary column and a flame ionization detector (FID).

Turnover number (TON) was calculated as the following formula:

$$\text{TON} = \Delta n_{\text{Benzene}} / n_{\text{Cu}}$$

$\Delta n_{\text{Benzene}}$: Converted benzene, mol;

n_{Cu} : Amount of active Cu sites, mol.

Kinetic Studies

In order to explain the origin of the extraordinary catalytic performance of the $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst for benzene selective oxidation to phenol, the kinetic studies were performed concerning benzene oxidation and phenol oxidation over diverse catalysts in the temperature range of 20–60 °C within a kinetic controlled regime. Reaction conditions: 20 mg of catalyst, 0.20 mL of benzene, 3.0 mL of H_2O_2 (30 wt%), 6 mL of CH_3CN , carried out for 1.5 h at 20 °C, 30 °C, 40 °C and 60 °C, respectively. The reaction rate (r) was calculated by dividing the number of the reacted benzene (phenol) by the

reaction time and the number of the supported active Cu atoms on HCNS. By plotting $\ln r$ as a function of $1/T$, an Arrhenius plot was achieved. With the slope and intercept of Arrhenius plot, the apparent activation barrier (E_a) and pre-exponential factor (A) for benzene oxidation and phenol oxidation over the catalysts were achieved.

Recyclability Test

To test the stability of single-atom $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst for benzene selective oxidation to phenol, the recycling experiment was performed. Typically, 20 mg of fresh $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst was applied in a 50 mL round-bottom glass flask. 6 mL CH_3CN , 5.2 mL H_2O_2 and 0.5 mL benzene was added and the flask was sealed carefully. The reaction was carried out at 60 °C for 12 h. After one cycle of reaction, solid catalyst was recovered by centrifugation, washed with ethanol and dried. The recovered catalyst was used for the next cycle. Products were analyzed by gas chromatograph.

Controlled experiments

To investigate the origin of the phenol selectivity increment over the recovered single-atom $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst, a rational controlled experiment was performed. Fresh $\text{Cu}_1\text{-N}_2/\text{HCNS}$ catalyst was firstly pretreated with hydrogen peroxide under the same condition as catalytic performance test except benzene was absent. Subsequently, solid catalyst was recovered by centrifugation, washed with ethanol for 3 times and dried. Then, 20 mg of hydrogen peroxide pretreated catalyst was applied in benzene selective oxidation to phenol as the same procedure in recycling test part. The final products were analyzed by gas chromatograph.

Comparative Trials of H_2O_2 Activation over $\text{Cu}_1\text{-N}_2/\text{HCNS}$ and $\text{Cu}_1\text{-N}_3/\text{HCNS}$

Typically, a certain amount of catalyst (0.046 mg of active Cu atoms, 6 mL of CH_3CN , 1.0 mL of benzene and 0.52 mL of H_2O_2 (30 wt%) were mixed in a 50 mL round-bottom glass flask and sealed carefully. Then the reaction was carried out at 60 °C in a water bath kettle with magnetic stirring for a period of time. After the reaction was accomplished and the system cooled down to room temperature, products was extracted by dichloromethane. The remained H_2O_2 was titrated by indirect iodometry method.

The conversion of H_2O_2 was calculated according to the following formula:

$$X_{\text{H}_2\text{O}_2} = 100\% \times (n_{\text{H}_2\text{O}_2}^0 - n_{\text{H}_2\text{O}_2}^1) / n_{\text{H}_2\text{O}_2}^0$$

$X_{\text{H}_2\text{O}_2}$: H_2O_2 conversion;

$n_{\text{H}_2\text{O}_2}^0$: the initial molar quantity of H_2O_2 ;

$n_{\text{H}_2\text{O}_2}^1$: the final molar quantity of H_2O_2 after reaction.

The effective utilization rate of H_2O_2 ($U_{\text{H}_2\text{O}_2}$) was calculated according to the following formula:

$$U_{\text{H}_2\text{O}_2} = 100\% \times (\Delta n_{\text{Benzene}} / \Delta n_{\text{H}_2\text{O}_2})$$

$\Delta n_{\text{Benzene}}$: Converted benzene, mol;

$\Delta n_{\text{H}_2\text{O}_2}$: Converted H_2O_2 , mol.

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