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Aerobic oxidation of fluorene to fluorenone over Co-Cu bimetal oxides

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Oxidation of sp³ C-H bonds has attracted increasing attention, and the aim of our work is to prepare catalysts for oxidation of sp³ C-H bonds using O₂ without initiator. In this paper, a series of Co-Cu bimetal oxides with different Co/Cu ratio were synthesized by sol-gel method and texted for catalytic oxidation of fluorene to fluorenone using molecule oxygen as oxidant in the absence of radical initiator. The best catalytic performance was achieved over $Co_{0.7}Cu_{0.3}$ catalyst and the catalysts could be reused without significant losing of the catalytic activity. Characterization results indicated that part of Cu entered the Co_3O_4 lattices, leading to more high-valence metal ions sites (Co^{3+} and Cu^{2+}) and surface oxygen species (O_2^{-2} , $O_2^{2^2}$, O^{-}) as well as promoted redox ability, which all enhanced the catalytic activity. In addition, the catalysts were also efficient for the oxidation of other benzylic C-H containing aromatic hydrocarbons such as tetralin, indan, diphenylmethane and ethylbenzene.

1. Introduction

Fluorenone is an important chemical intermediate that has been widely used in organic solar cells,¹ polymer,² dye,³ pharmacy,⁴ electrochemistry,⁵ and optical materials⁶. Compared with methods of fluorenone synthesis using raw materials instead of fluorene,⁷⁻¹² direct oxidation of fluorene to fluorenone is an economic and environmental friendly route, which employed the abundant and cheap fluorene, an important component in coal tar form coal pyrolysis, as raw material. As a result, the process has attracted much interest.

Fluorene could be oxidized through gas-phase reactions or liquid-phase reactions. The gas-phase oxidation of fluorene to fluorenone is carried out under high temperature,^{13,14} while the liquid-phase oxidation processes can be performed at relatively mild conditions. However, sacrificial oxidizing reagents, such as NaIO₄,¹⁵ permanganate,¹⁶ tert-butyl hydroperoxide,17 phenylmethylsulfoxide,¹⁸ polymeric iodosobenzene¹⁹ etc. are employed which are normally expensive and may generate wastes. Some of these oxidants also hard to separate i.e. they are not deemed "green". As a result, molecular oxygen has been used because it is economic, abundant, and environmentally friendly. Many homogeneous catalysts such as KOtBu,²⁰ NHPI,²¹ and organic-metal complex²² have been reported. Despite the high conversion, these homogeneous catalysts suffer from the poor recyclability as well as difficulty for separation from the products.²³ As a result,

59 60 heterogeneous catalyst, such as Cu-CuFe₂O₄@HKUST-1,²⁴ and Au-pDA-rGO,²⁵ have been used which showed high catalytic activity. However, radical initiator such as NHPI is needed in the reaction systems. Therefore, development of high efficient heterogeneous catalysis system without addition of radical initiator or other additives is needed. Transition metal oxides are promising options which are relatively cheap and highly active for benzylic C-H bonds oxidation include fluorene oxidation. Opembe et al.26 prepared manganese oxide octahedral molecular sieves for fluorene oxidation to fluorenone. They proposed that manganese ions of various valence (Mnⁿ⁺, n=2, 3, 4), oxygen species (O_2^-, O_2^-, O_2^-) , and molecular oxygen dissolved in the reaction system are involved in the oxidation. Zhang et al.²⁷ reported that allylic or benzyl C-H bonds containing hydrocarbons include fluorene could be oxidized to ketones over MnCeOx solid solutions. The abundant oxygen species, strong ability for activation of oxygen molecules and rich porosity of the catalyst favor the reaction.

 Co_3O_4 is a mixed valence transition metal oxide which contains Co^{3+} occupying the octahedral sites and Co^{2+} ions occupying the tetrahedral sites with the mobile oxygen inside the spinel structure.²⁸ So, it is more active for oxidation of $CO,^{29-32}$ formaldehyde,³³ volatile organic compounds,³⁴ and alcohols³⁵ because of the excellent redox activity.³⁶ CuO, as transition metal oxide, has also been used for oxidation reactions such as CO oxidation,³⁷⁻⁴⁰ alcohol oxidation,^{41,42} oxidation of formaldehyde.⁴³ Doping of CuO to Co_3O_4 showed better performance than Co_3O_4 due to the synergetic effects between cobalt and copper ions.^{44,45} However, the oxidization of fluorene to fluorenone or other benzylic C-H bonds using

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molecular oxygen as oxidant over Co-Cu bimetal oxides, as far as we know, is rarely reported.

In this context, Co-Cu bimetal oxides were prepared and used for synthesis of fluorenone by fluorene oxidation in the absence of initiator which showed high conversion and selectivity. The relationship of physical and chemical properties, especially high-valence metal ions site (Co^{3+} and Cu^{2+}) and surface oxygen species, and the catalytic performance was discussed. Moreover, the free radical quenching experiment was conducted to exploring the possible reaction mechanism. Substrate scope and reusability were also studied to understand the application prospects of this protocol.

2. Experimental

2.1. Catalysts preparation

All reagents were analytical grade and used without further purification. $Co_{1-x}Cu_xO_y$ (x=0.1, 0.3, 0.5, 0.7) catalysts were synthesized via sol-gel method using $Co(NO_3)_2$ · GH_2O and $Cu(NO_3)_2$ · $3H_2O$ as precursors. Typically, 400 mL of ethanol solution containing $Co(NO_3)_2$ · GH_2O and $Cu(NO_3)_2$ · $3H_2O$ (0.2 mol L⁻¹) was prepared, 200 mL solution of citric acid (0.2 mol L⁻¹) in ethanol was then introduced under vigorously stirring. The mixture was stirred for 24 h at room temperature and heated to 80 °C to remove the solvent to obtain foam-like gel. The asobtained porous gel was thus dried at 80 °C for 24 h followed by calcination at 500 °C for 4 h under air to obtain the Co-Cu bimetal oxides catalysts. The as-prepared Co-Cu bimetal oxides catalysts were named as $Co_{1-x}Cu_x$ (x=0.1, 0.3, 0.5, 0.7).

2.2. Characterization of catalysts

The X-ray diffraction (XRD) patterns of catalysts were conducted on a Bruker D8 Advance (Germany) diffract-meter with a Cu K α radiation. The diffraction patterns of catalysts were recorded from 10° to 80° at a scanning speed of 2° min⁻¹. Phases of catalysts were identified by comparison with the joint committee on powder diffraction standards (JCPDS) database cards.

The morphology of samples was characterized using transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) on JEM-2100F equipment with an accelerating voltage of 200 kV.

Nitrogen adsorption and desorption experiments were measured at -196 °C using a Micromeritics Tristar II (3020) apparatus. The catalysts were degassed at 120 °C for 8 h under vacuum before the measurement. The specific surface areas of catalysts were calculated according to the Brunauer-Emett-Teller (BET) methods and Barrett-Joyner-Halenda (BJH) method was employed to determine the pore size distributions. Inductively coupled plasma emission spectrometry (ICP) was

completed on Thermo iCAP6300 spectrometer.

X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Fisher Scientific ESCALAB 250Xi spectrometer equipped with Al K α radiation source to investigate the chemical states of surface species. The binding energies of all

the elements were corrected by the C 1s line at 284,8, eVe from adventitious carbon.

The reducibility of the Co_{1-x}Cu_x catalysts was studied by H₂ temperature reduction (H₂-TPR). In a typical experiment, 50 mg of catalysts was loaded in a U-shape tube quartz reactor blocked by silica wool. The reactor was purged under Ar (50mL min⁻¹) and per-treated at 500 °C for 1 h to remove the physically adsorbed molecules. Then the reactor cooled down to room temperature under the same atmosphere. Subsequently, the gas passing through the reactor was switched to 5% H₂/Ar at flow rate of 50 mL min⁻¹ until the thermal conductivity detector (TCD) signal was flat and then the sample was heated to 500 °C with a rate of 10 °C min⁻¹.

 O_2 temperature-programmed desorption (O_2 -TPD) was performed on the same device used for H₂-TPR. For O_2 -TPD, 200 mg catalyst was placed in the U-shape tube quartz reactor and pre-treated under Ar flow with a rate of 50 mL min⁻¹ at 500 °C for 1 h. Then adsorption of O_2 was performed at room temperature with O_2 (99.999%, 50 mL min⁻¹) for 1 h followed by purging with pure Ar (50 mL min⁻¹) for 1 h at room temperature to remove the unabsorbed and physisorbed O_2 molecules. The desorption process was performed under Ar flow with a rate of 50 mL min⁻¹ from room temperature to 500 °C at a heating rate of 10 °C min⁻¹ and the desorbed O_2 was detected by a TCD.

Fourier transform Infrared spectra (FT-IR) of the prepared catalysts were recorded by the conventional KBr pellet method. FT-IR measurement was carried out using a Nicolet NEXUS 470 FT-IR spectrometer in the range of 400-4000 cm⁻¹ at a resolution of 4 cm⁻¹.

Raman spectra of $Co_{1-x}Cu_x$ catalysts were recorded on LabRAM HR equipment, catalysts were probed using an argon laser excitation source operating at 532 nm and the scanned range was from 100-1000 cm⁻¹.

2.3. Catalytic tests

The catalytic oxidation of fluorene by molecular oxygen was carried out in a 100 mL stainless-steel autoclave equipped with a magnetic stirrer. Typically, 1 mmol of fluorene, 10 mL of cyclohexane and 100 mg of $Co_{1-x}Cu_x$ catalysts were loaded into the reactor. Then the reactor was sealed and purged with pure O_2 to replace the air for three times. The O_2 was then charged into the autoclave with the initial pressure of 1.0 MPa and heated to 110 °C for reaction with constantly stirring for 4 h. After reaction, the autoclave was put into ice water to quench the reaction. The catalyst was separated by centrifugation and the products were analyzed by gas chromatography (GC) equipped with a FID detector and an Agilent DB-5 column. Acetophenone was used as internal standard.

3. Results and discussion

3.1. Structural and textural properties of the catalysts

3.1.1. X-ray diffraction (XRD)

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Fig. 1 XRD patterns of $Co_{1-x}Cu_x$ catalysts

XRD patterns of Co₃O₄, Co_{1-x}Cu_x and CuO catalysts were shown in Fig. 1. The pure cobalt and copper oxide were identified as Co_3O_4 and CuO, respectively. Diffraction peaks of Co_3O_4 and CuO were detected for the $Co_{1-x}Cu_x$ catalysts and the intensities of each metal oxide peaks increased with the increasing of the ratio of Cu to Co, indicating the formation of metallic oxides. No CuO phase was found for Co_{0.9}Cu_{0.1} probably because the copper ions have entered the Co₃O₄ lattice to form CuCo2O4. However, it is very difficult to distinguish the $CuCo_2O_4$ and Co_3O_4 due to the overlapping of the diffraction peaks.⁴⁶ CuO phase appeared when the copper ratio was higher than 0.3. Compared with physical mixture of $\text{Co}_{0.7}\text{-}\text{Cu}_{0.3}$ catalyst, $\text{Co}_{0.7}\text{Cu}_{0.3}$ catalyst showed lower signals intensities, suggesting the smaller particle sizes and better dispersions of Cu and Co. Meanwhile, for physical mixture of $Co_{0.7}$ - $Cu_{0.3}$, the intensities ratio of Co_3O_4 /CuO was higher than that of Co_{0.7}Cu_{0.3}, probably due to the fact that part of copper ions entered the Co_3O_4 lattice leading to weakened CuO signals e.g. the interaction between cobalt and copper was improved.

3.1.2. Transmission electron microscope (TEM)

TEM images of the Co_3O_4 , CuO and $Co_{1-x}Cu_x$ were shown in Fig. S1. All the samples showed the agglomeration of particles with irregular shape. Furthermore, with the increased of copper content, the particle size increased especially when the copper content was higher than 0.5, which might lead to decreased specific surface area of the samples. High resolution TEM (HRTEM) images (Fig. S1) showed that lattice fringes of 0.286 nm, 0.467 nm, 0.244 nm, and 0.253 nm, 0.232 nm were presented in samples, which were in good agree with the spacing of Co_3O_4 (220), (111), (311), and CuO (002), (111), respectively.^{36,47,48}

3.1.3. N₂ adsorption-desorption

The N₂ adsorption-desorption isotherms and BJH pore diameter

able 1 Texture properties of Co _{1-x} Cu _x catalysts View Article Onli DOI: 10 1039/C9NJ00499					
Catalysta	S _{BET}	Pore volume	Average pore		
Catalysts	(m² g-1)	(cm ³ g ⁻¹) ^a	size (nm) ^b		
Co ₃ O ₄	12.1	0.078	25.7		
$Co_{0.9}Cu_{0.1}$	11.8	0.064	21.5		
Co _{0.7} Cu _{0.3}	11.3	0.060	21.2		
Co _{0.5} Cu _{0.5}	10.5	0.058	22.2		
Co _{0.3} Cu _{0.7}	7.7	0.041	21.3		

a Total pore volume measured at $p/p_0=0.99$.

CuO

Co_{0.7}-Cu_{0.3} mixed

b The pore diameter calculated from the desorption branch of the isotherm using the BJH method.

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Fig.2 a) N_2 sorption isotherms, and b) pore size distribution curves: BJH of samples.

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distribution curves of the samples were shown in Fig. 2. The pore structure parameters were summarized in Table 1. The isotherms of samples gave similar characteristics of type II profile, suggesting the existence of mesopores and macropores.⁴⁴ Hysteresis loops also existed except CuO, indicated the existence of mesoporous.⁴⁹ The pore size distribution curves also confirmed the formation of mesopores and macropores of samples. As shown in Table 1, the BET surface area of Co_3O_4 was 12.1 m² g⁻¹ while that of CuO was only 3.2 m² g⁻¹. It was obvious that for the samples with copper content between 0.1 and 0.5, the BET surface area of the catalysts did not change significantly. However, the specific surface area decreased sharply when the copper content was higher than 0.5, and the results consist with TEM results. Compared with physical mixture of Co_{0.7}-Cu_{0.3} catalyst, the Co_{0.7}Cu_{0.3} sample had larger BET surface, indicating that sol-gel method might lead to larger specific surface area. Moreover, the pore volume of the samples decreases with the doping of Cu while the average pore size was almost the same.

3.2. Chemical states and redox behavior

3.2.1 Inductively coupled plasma emission spectrometry (ICP)

As shown in Table S1, the real Cu/(Co+Cu) molar ratio measured by ICP was almost identical to the feed molar ratio of Cu/(Co+Cu), indicating little loss of metal element during the process of catalysts preparation.

3.2.2. X-ray photoelectron spectroscopy (XPS)

The XPS profiles of the samples were shown in Fig. 3 and the contents of surface element, oxygen species and Co^{3+}/Co^{2+} were summarized in Table 2. For the Co_3O_4 and $Co_{1-x}Cu_x$ catalysts, the binding energies of Co $2p_{3/2}$ and Co $2p_{1/2}$ were observed at 779.8 ± 0.2 and 794.8 \pm 0.2 eV, respectively. The Co 2p spin-orbital splitting value were 15.0 \pm 0.1 eV, indicating that Co_3O_4 and Co^{3+} presented on the surface of the catalysts. $^{50\text{-}52}$ Co $2p_{1/2}$ and Co $2p_{3/2}$ peaks could be fitted into two peaks e.g. the peaks at around 779.9 eV and 794.9 eV were assigned to octahedral Co³⁺, while the peaks at around 781.5 eV and 796.5 eV were attributed to tetrahedral $Co^{2+}.^{28,53}$ The Co^{3+}/Co^{2+} of $Co_{1-x}Cu_x$ catalysts was higher than that of pure Co_3O_4 , revealing that Cu doping could increase the Co^{3+}/Co^{2+} ratio by occupation of tetrahedral sites to form $\mbox{CuCo}_2\mbox{O}_4.^{45}$ For the samples with copper content higher than 0.3, the Co³⁺/Co²⁺ ratio of Co1-xCux was almost the same. Combined with the XRD results, the amount of copper ions entering Co_3O_4 lattices reached maximum for $Co_{0.7}Cu_{0.3}$.

Cu 2p spectra (Fig. 3b) of CuO and Co_{1-x}Cu_x catalysts exhibited two major peaks at about 934.2 (Cu $2p_{3/2}$) and 954.0 eV (Cu $2p_{1/2}$), respectively.^{45,52} Shake-up satellites on the high energy sides might arise from a ligand-metal 3d charge transfer. The satellite peaks between Cu $2p_{3/2}$ peak and Cu $2p_{1/2}$ peak as well as the Cu 2p spinorbital splitting values of 19.9 ± 0.1 eV all confirmed the presence of Cu²⁺ on the surface of the catalysts.^{45,52,54} Wider separation between the Cu 2p_{3/2} line and its corresponding satellite peak of $Co_{0.9}Cu_{0.1}$ indicated the decreased covalent character of the Cu-O, in which all the copper ions entered the Co_3O_4 lattices. This result also mightily suggested the CuO phase segregation at the surface of Co_{1-x}Cu_x oxides.⁵⁵ The Cu 2p_{3/2} peaks of Co_{0.9}Cu_{0.1} and Co_{0.7}Cu_{0.3}







Fig. 3 XPS spectra of $Co_{1-x}Cu_x$ catalysts a) Co 2p spectra b) Cu 2p spectra and c) O 1s spectra

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Table 2 Statistics of the XPS survey

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Sample	Surface element molar ratio (%)			O 1s (%)		Co 2p (%)		Cu 2p		
	Со	Cu	0	OI	O _{II}	O _{III}	C0 ²⁺	Co ³⁺	Co ³⁺ /Co ²⁺	Cu ²⁺ /(Cu ⁺ +Cu ⁰)
Co ₃ O ₄	31.76	-	68.24	52.78	34.70	12.52	50.96	49.04	1.04	-
$Co_{0.9}Cu_{0.1}$	22.45	10.22	67.33	50.08	38.49	11.42	42.30	57.70	1.36	3.49
Co _{0.7} Cu _{0.3}	19.30	14.90	65.80	49.08	40.68	10.24	39.77	60.23	1.51	7.95
Co _{0.5} Cu _{0.5}	15.32	20.44	64.24	49.48	40.39	10.13	40.08	59.92	1.50	-
Co _{0.3} Cu _{0.7}	9.55	27.26	63.19	49.37	40.24	10.39	39.52	60.48	1.53	-
CuO	-	41.76	58.24	51.41	36.50	12.09	-	-	-	-
Co _{0.7} -Cu _{0.3} mixed	25.24	6.80	67.96	52.53	35.09	12.38	50.41	49.59	1.03	-

could also be fitted into two peaks. The peaks at around 932.1 eV might correspond to Cu⁺/Cu⁰, and the peaks at around 934.1 eV were assigned to Cu2+, respectively.37,38 The Cu2+ to Cu+/Cu0 ratio of $\text{Co}_{0.7}\text{Cu}_{0.3}$ higher than that of $\text{Co}_{0.9}\text{Cu}_{0.1}\text{,}$ and with the copper content increased, only one peak at around 934.1 eV was found, indicating little Cu⁺/Cu⁰ species in the samples due to the decreased of cobalt content as well as increased of copper content led to copper exists mainly in the form of CuO. As shown in Fig. 3b and Table 2, for Co_{0.9}Cu_{0.1} and Co_{0.7}Cu_{0.3}, higher Cu 2p binding energy compared with pure CuO implied the low electron cloud as the copper ions entered Co₃O₄ lattice. Moreover, binding energy of Co 2p and O 1s of Co_{1-x}Cu_x slightly shifted toward lower values, probably due to the electron transfer from Cu to the oxygen and cobalt, which may be conducive to the oxygen activation i.e. the adsorbed molecular oxygen could obtain electrons easier to form surface oxygen species (O_2^-, O_2^{-2}, O^-) .

Fig. 3c showed the O 1s XPS spectra of $Co_{1-x}Cu_x$ catalysts i.e. the O 1s peaks could be deconvolved into three components peaks. The peaks (O₁) at low binding energy (529.7-529.9 eV) attributed to the lattice oxygen species (O²⁻), the shoulder peaks (O₁₁) at



Fig. 4 H₂-TPR profiles of Co_{1-x}Cu_x catalysts

approximately 531.3 eV assigned to surface oxygen species (O_2^- , O_2^{2-} , O^-) and the peaks (O_{III}) at 533.0 eV to 533.5 eV corresponded to the chemisorbed water. ^{27,50,56,57} With the doping of copper, the amount of O_{II} increased which means the increasing of surface oxygen species. Higher percent of surface oxygen species (O_2^- , O_2^{2-} , O^-) of Co_{1-x}Cu_x than that of Co₃O₄ and CuO also suggested more surface defects of Co_{1-x}Cu_x resulted from doping of copper.²⁸

3.2.3. Hydrogen temperature programmed reduction (H₂-TPR)

Fig. 4 showed the H_2 -TPR profiles of the $Co_{1-x}Cu_x$ catalysts. Two reduction peaks were distinguished for the TPR curve of Co₃O₄. The prominent peak centered at 411 °C and a pronounced shoulder at lower temperature implied that the reduction process was composed of at least two major steps. The former step was characterized by the reduction of Co³⁺ to Co²⁺, whereas the latter was assigned to the reduction of Co²⁺ to Co^{0,50} A prominent peak accompanied by a shoulder was observed for H₂-TPR profile of CuO. The shoulder at low reduction temperature was assigned to the reduction of CuO to Cu₂O, while the prominent peak was assigned to the reduction of Cu₂O to metallic Cu^{0,58} The reduction peaks of $Co_{1-x}Cu_x$ catalysts showed a significant shift to lower temperatures compared with pure Co₃O₄ and CuO indicating that high-valence ions in Co_{1-x}Cu_x were easier to obtain electrons than that in pure Co_3O_4 and CuO. Among all the $Co_{1-x}Cu_x$ catalysts, $Co_{0,7}Cu_{0,3}$ had the lowest prominent peak center, namely, the reducibility had the most significant improvement.

3.2.4. Oxygen temperature programmed desorption (O₂-TPD)

O₂-TPD profiles of different samples were shown in Fig. 5. Co₃O₄ had three desorption peaks at around 100 °C, 200 °C and 400 °C, respectively. CuO showed two peaks at the ranges of 80-120 °C and 120-250 °C. Generally, the activation of molecular oxygen underwent the following process: O₂ (ad) → O₂⁻ (ad) → O⁻ (ad) → O²⁻ (lattice).⁵⁹ The peak corresponding to desorption temperature at the ranges of 80-120 °C was assigned to molecular oxygen specie adsorbed on oxygen vacancies while the peak at the temperature range of 120-450 °C was attributed to surface oxygen ions.⁵⁰ The





Fig. 5 O_2 -TPD profiles of $Co_{1-x}Cu_x$ catalysts

 $Co_{0.9}Cu_{0.1}$, $Co_{0.7}Cu_{0.3}$ and $Co_{0.5}Cu_{0.5}$ exhibited larger oxygen desorption peak areas at 80-120 °C and 120-450 °C in comparison to Co_3O_4 and CuO oxide, suggesting that $Co_{1-x}Cu_x$ catalysts had better oxygen adsorption capacity and surface oxygen ions i.e. greater ability of oxygen adsorption and oxygen activation which favored the oxidation reaction.

3.2.5. FT-IR

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The FT-IR spectra of $Co_{1-x}Cu_x$ catalysts were shown in Fig. 6. In the range of 400 to 4000 cm⁻¹, all the samples had broad peaks at 3480 cm⁻¹ due to the stretching vibrations of O-H bond. The band at 1630 cm⁻¹ was attributed to the adsorption of water.^{33,60} The spectra of CuO presented two distinct absorption peaks at 582 cm⁻¹ and 536 cm⁻¹ which were assigned to the stretching vibrations of Cu(II)-O.⁴⁷ The spectra of Co₃O₄ and Co_{1-x}Cu_x catalysts presented two distinct absorption peaks at approximately 660-667 cm⁻¹ and 579-565 cm⁻¹, respectively. The band located at about 660-667 cm⁻¹ was assigned to Co-O stretching vibrations from Co²⁺ in tetrahedral sites, while the band at about 579-565 cm⁻¹ was attributed to the bridging vibration of O-Co-O bond of the Co³⁺ in octahedral sites.⁶¹⁻⁶³ The FT-IR spectra also indicated the formation of Co₃O₄ spinel oxide.⁶¹ With doping of Cu, the peak of Co-O stretching vibration shifted to 660 cm⁻¹ and almost did not change with the change of Cu content. The peak of bridging vibration of O-Co-O bond also had a red shift as the Cu content increased, indicating the weakened Co-O bonds which favored the Co and O to participate in the oxidation reaction. The result also confirmed that the copper doped into the spinel phase Co₃O₄.⁴⁸ No obvious peak assigned to the Cu-O bond was observed probably due to that the peak of Co-O stretching vibration overlapped with the Cu-O stretching vibration peak.⁶⁴

3.2.6. Raman spectroscopy

To explore the structure of $Co_{1-x}Cu_x$ catalysts, Raman spectra were collected (Fig. 7). For Co_3O_4 , the bands at 192, 513 and 611 cm⁻¹ were assigned to the F_{2g} mode. The band at482 cm⁻¹ was assigned to E_g mode and the band at 692 cm⁻¹ was assigned to A_{1g} mode. All







Fig. 7 Raman spectra of Co_{1-x}Cu_x catalysts

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these bands were attributed to spinel-type $Co_3O_4^{50,65}$ i.e. the A_{1g} mode corresponded to the vibration of octahedral site of Co_3O_4 lattice, while the F_{2g} and E_g modes were related to the tetrahedral and octahedral sites.⁶⁶ CuO showed three Raman active peaks i.e. the peak at 275 cm⁻¹ was attributed to A_g mode, while the peaks at 329 and 613 cm⁻¹ were assigned to B_g mode, which corresponding to CuO.⁵⁸ Co_{1-x}Cu_x catalysts showed similar Raman patterns with slightly red shift compared with Co₃O₄ and physical mixed Co_{0.7}-Cu_{0.3} catalyst, revealing the presence of lattice strains, heterojunctions, and sample variability which might lead to defects.^{67,68}

3.3. Catalytic activity studies

3.3.1. Catalytic performance

The catalytic activity of $Co_{1-x}Cu_x$ catalysts towards the oxidation of fluorene were shown in Table 3. It could be seen that all the $Co_{1-x}Cu_x$ catalysts showed higher catalytic activity than Co_3O_4 and CuO, among which the $Co_{0.7}Cu_{0.3}$ catalyst had the best performance (Table 3, Entries 2-7). Physical mixed $Co_{0.7}-Cu_{0.3}$ catalyst (Table 3, Entry 8) had lower catalytic activity than $Co_{3}O_4$.

Doping of CuO into the Co₃O₄ caused changes of chemical states and surface properties, leading to the change of catalytic performance. According to the literature, Co³⁺ ions occupying the octahedral sites in Co_3O_4 were beneficial for CO oxidation,^{29,69} formaldehyde oxidation,³³ and so on. The proposed mechanism (Scheme 1) also suggested that high-valence metal ions, namely Co³⁺ and Cu²⁺, played a key role in this reaction e.g. strong abilities to capture electrons of high-valence metal ions were more conducive to produce carbon center free radicals that initiated the free radical chain reactions. Co2+ occupying the tetrahedral sites, which could not be oxidized to Co3+ in spinel Co3O4 structure, showed poor oxidation activity for fluorene oxidation. The fact that Cu^{2+} entered the Co_3O_4 lattices and replaced the Co^{2+} occupying the tetrahedral sites led to increased Co3+/Co2+ as well as more highvalence metal active sites, resulting in better performance than Co_3O_4 . However, CuO separated from $Co_{1-x}Cu_x$ may not favor the oxidation reaction, due to the lower catalytic activity of CuO. When the copper content was higher than 0.5, the BET surfaces decreased, leading to less exposed high-valence metal active sites and more separated CuO, which all had negative influence for the oxidation process.

According to the proposed reaction mechanism, surface oxygen species (O_2^{-}) were another major role which involved in the free radical chain initiation. O 1s XPS results revealed the increased surface oxygen species ratio with the doping of copper, implying more O_2^{-} on the surface which was favorable for the oxidation reaction. As a result, $Co_{0.7}Cu_{0.3}$ with both high surface oxygen species and BET surface showed better catalytic activity.

Co₃O₄ had been proposed to accompany redox cycles involving reduction and oxidation of octahedral Co³⁺ site in the catalytic oxidation⁷⁰ e.g. the redox ability had significant influence on the oxidation reaction. In this study, doping of copper in Co₃O₄ favored the reduction of Co³⁺ to Co²⁺ and Cu²⁺ to Cu⁺ i.e. all the Co_{1-x}Cu_x catalysts had lower reduction temperature than Co₃O₄ and CuO. The Co_{0.7}Cu_{0.3} catalyst with the lowest reduction temperature suggested the highest redox ability and thus the highest oxidation activity.

Table 3 The catalytic performance of	foxidation of fluoreneapyeronline
Co _{1-x} Cu _x catalysts	DOI: 10.1039/C9NJ00499H

Entry	Catalysts	Т	t	Conversion	Selectivity
		(°C)	(h)	(%)	(%)
1	Blank	110	4	3	98
2	Co ₃ O ₄	110	4	50	99
3	$\mathrm{Co}_{0.9}\mathrm{Cu}_{0.1}$	110	4	63	99
4	Co _{0.7} Cu _{0.3}	110	4	66	99
5	$Co_{0.5}Cu_{0.5}$	110	4	62	99
6	$Co_{0.3}Cu_{0.7}$	110	4	54	99
7	CuO	110	4	34	99
8	Co _{0.7} -Cu _{0.3} mixed	110	4	43	99
9 ª	$Co_{0.7}Cu_{0.3}$	110	4	2	98
10 ^b	Co _{0.7} Cu _{0.3}	110	4	1	92

Reaction conditions : fluorene (1 mmol), catalyst (100 mg), cyclohexane (10 mL), O_2 (initial pressure 1 MPa) a With 0.2 mmol of BHT

b With 0.2 mmol of p-benzoquinone

In addition, surface defects of Co_3O_4 were beneficial for the catalytic oxidation reaction.^{28,71} The XPS results of O 1s and Raman spectra revealed that $Co_{1-x}Cu_x$ catalysts exhibited more surface defects. Molecular oxygen species adsorbed on oxygen vacancies can be converted to oxygen ions $(O_2^-, O_2^{2^-}, O^-)$ by capture electrons from metal oxides. Doping of Cu was conducive to oxygen activation to produce surface oxygen absorbed on oxygen vacancies to form surface oxygen species which promoted the catalytic performance.

3.3.2. Optimization of reaction conditions

To understand the effect of reaction conditions on the catalytic performance, reaction parameters included reaction time, reaction temperature, initial pressure of O₂ and amount of catalyst were studied over Co_{0.7}Cu_{0.3}. The oxidation reaction was extremely dependent on the reaction time (Fig. 8a). A gradual increase in the conversion from 66% to 99% was found with the reaction time increased from 4 h to 12 h. Longer reaction time could result in higher conversion. While the selectivity to fluorenone slight decreased form 99% to 92%. With the reaction temperature increased from 90 °C to 130 °C, conversion of fluorene increased rapidly from 25% to 99% (Fig. 8b). However, high reaction temperature (>120 °C) led to decreased selectivity of fluorenone (94% at 120 °C and 86% at 130 °C) probably due to the over oxidation. Low initial pressure of O₂ did not favor the reaction (Fig. 8c). With the initial pressure of O_2 increased from 0.2 MPa to 1.8 MPa, conversion of fluorene increased from 47% to 97%. The selectivity changed little until the initial pressure of O₂ increased to 1.4 MPa while decreased to 92% when the initial pressure of O₂ was 1.8 MPa. More catalysts let to higher conversion of fluorene, mainly

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Fig. 8 Effect of reaction conditions on fluorene oxidation to fluorenone over $Co_{0.7}Cu_{0.3}$, reaction condition: 1 mmol fluorene, 10 mL cyclohexane, and a) 100 mg catalyst, O_2 initial pressure 1 MPa at 110 °C; b) 100 mg catalyst, O_2 initial pressure 1 MPa for 8 h; c) 100 mg catalyst, reacted at 110 °C for 8 h; d) O_2 initial pressure 1 MPa, reacted at 110 °C for 8 h

due to more introduced active sites (Fig. 8d). Meanwhile, no significant change in the selectivity was observed. However, the increase of conversion slowed down when the amount of catalysts was higher than 100 mg. As a result, the best catalytic performance was achieved with 88% conversion of fluorene and 99% selectivity to fluorenone under the reaction condition of 100 mg of catalysts, 110 °C, 8 h and 1 MPa of initial O₂ pressure.

3.3.3. Substrate scope

To establish the general applicability of the Co_{1-x}Cu_x catalysts, various aromatic hydrocarbons containing benzylic C-H bonds were subjected to oxidation reaction and the results were shown in Table 4. Appropriate reaction conditions were employed for the oxidation of aromatic hydrocarbons. Co_{0.7}Cu_{0.3} catalyst was found to be effective in the oxidation of aromatic hydrocarbons over which ethylbenzene conversion was 22% (Table 4, Entry 1) with the 1phenylethyl alcohol and acetophenone as the main product. For indane and tetralin oxidation, much higher conversion and selectivity to benzylic alcohols and benzylic ketones were obtained (Table 4, Entry 2, 3). Moreover, diphenylmethane with two benzenes rings could also be oxidized to diphenylmethanone with high selectivity (Table 4, Entry 4). Therefore, $Co_{0.7}Cu_{0.3}$ could be considered as general catalysts for aerobic oxidation of benzylic sp³ C-H bonds.

3.3.4. Heterogeneity test

Leaching experiment was performed to ascertain the nature of the catalytic reaction and the results were shown in Fig. 9. The $Co_{0.7}Cu_{0.3}$ catalyst was filtered from the reaction system after 4 h and the filtrate was subsequently reacted under the same conditions. The result showed only a slight increase after the catalyst was filtered, which revealed the heterogeneity of the catalyst. Furthermore, ICP analysis of the liquid phase showed no significant metal ions leaching (< 0.1 ppm), which further confirmed that the catalytic system was heterogeneous.

3.3.5. Reusability

The reusability of the $\text{Co}_{1\text{-}x}\text{Cu}_x$ oxides catalysts for fluorene

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nzenes h selec nsidered l bonds **.4. Het** aching e alytic r _{0.7}Cu_{0.3} d the nditions alyst w alyst. F nificant it the ca **.5. Reu** e reusa

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oxidation was also studied (Fig. 10). After completion of each reaction, the catalyst was separated by centrifugation, washed with ethanol for several times, and then dried at 80 °C overnight. The results revealed that the catalytic activity for $Co_{0.7}Cu_{0.3}$ catalyst had a slight drop after five cycles, indicating the good reusability. The XRD and FT-IR results (Fig. S2, S3) of the used catalyst matched well with the fresh catalyst, the morphology (Fig. S4) of the used catalysts had not obvious changes, implying that the crystal structure of catalyst was stable. While the XPS results (Fig. S5, Table S2) of the used catalysts showed more of low-valence metal ions

exist on the surface of catalysts after reaction, probably due to the fact that high-valence ions were reduced. XPS results also showed more surface oxygen species on the surface of used catalysts, probably because the molecular oxygen was activated to surface oxygen species during the reaction. The H₂-TPR results (Fig. S6) showed a slight shift of reduction peaks, which not favor for the reactions. The shoulder peaks corresponding to the reduction of $Co^{2+}/Cu+$ to Co^{0}/Co^{0} became stronger after reaction, indicating more low-valence metal ions presence after reaction which was consistent with the XPS result.







Fig. 10 Reusability test of the $Co_{0.7}Cu_{0.3}$

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Scheme 1 Proposed mechanism for the catalytic oxidation of fluorene

3.4. Reaction mechanism

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In order to probe the pathway of fluorene oxidation to fluorenone, 2,6-di-tert-butyl-4-methylphenol (BHT) and p-benzoquinone were used as carbon-centered radical guencher,⁷² and peroxyl radical quencher,⁷³ respectively. As shown in Table 3, the presence of BHT and p-benzoquinone inhibited the oxidation reaction. These results strongly suggested the involvement of carbon-centered radical and peroxyl radical as the active species for the oxidation process. The reaction pathway was similar to the fluorene oxidation mechanism proposed by Opembe et al.²⁶ Initially, fluorene interacted with $Co_{1-x}Cu_x$ catalysts. A hydrogen atom at the benzylic position was abstracted and the high-valence metal ion was reduced by obtaining an electron. The surface oxygen species (O_2) obtained a proton to form hydrogen peroxide radical (HOO·). Meanwhile, the fluorene converted to fluorene radical. The reduced low-valence metal ion could be oxidized by molecular oxygen e.g. the oxygen got an electron from low-valence metal ions to form surface oxygen ions (O_2^{-}) . The fluorene radical interacted with molecular oxygen to form fluorene peroxyl radical which then attacked another fluorene to abstract hydrogen atom and converted to fluorene hydroperoxide. Another fluorene lost hydrogen atom and became fluorene radical. Fluorene radical could combine with HOO· to form fluorene hydroperoxide. Finally, fluorene hydroperoxide decomposed into fluorenone, the target product, and H₂O.

4. Conclusions

Co-Cu bimetal oxides were prepared by sol-gel method which showed better performance for catalytic oxidation of fluorene to fluorenone than pure Co_3O_4 and CuO. Upon doping of copper, Cu^{2+} partially entered the Co_3O_4 lattice and replaced the Co^{2+} at the tetrahedral sites, leading to increased amount of high-valence metal ions (Co^{3+} and Cu^{2+}) and surface oxygen species (O_2^{-} , O_2^{2-} , O^{-}) which promoted the initiate free radical chain reaction. Doping of copper also promoted the redox ability of Co-Cu bimetal oxides, resulting easily redox cycles between Co^{2+} and Co^{3+} , which facilitated the catalytic oxidation process. Moreover, the optimized catalyst was also able to oxidize a series of benzylic C-H containing aromatic hydrocarbons including tetralin, indar?^{1:} Uphenylitethane, ethylbenzene with good conversion and selectivity. This study provided a promising protocol for benzylic C-H bond oxidation with economical and eco-friendly characteristics.

Conflicts of interest

There are no conflicts to declare.

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Aerobic oxidation of fluorene to fluorenone was achieved over Co-Cu bimetal oxides using O_2 as oxidant in the absent of radical initiator. Co-Cu bimetal oxides showed better catalytic performance than CuO and Co₃O₄.