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Comparative study of Cu-based bimetallic oxides for Fenton-like degradation of organic pollutants

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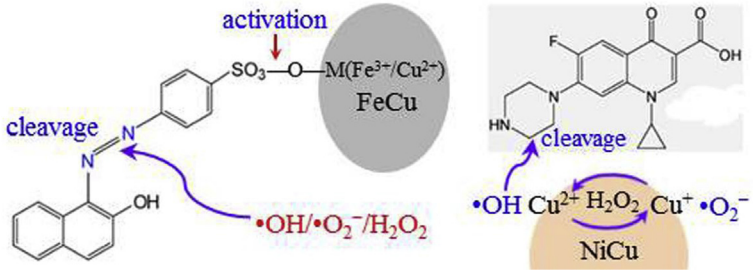
HIGHLIGHTS

- Fenton-like activities of Cu-based bimetallic oxides are compared.
- They exhibit different activity for the decomposition of H_2O_2 to active radicals.
- FeCu and NiCu exhibit high activity for Orange II and ciprofloxacin, respectively.
- Possible mechanism for the Fenton-like degradation of pollutants is discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to provide useful information for the rational design of effective Fenton-like catalyst, a series of Cu-based bimetallic oxides were synthesized and their Fenton-like performances for the degradation of Orange II and ciprofloxacin were compared. The structure, chemical oxidation state, surface charge property and redox ability of the catalysts were also investigated by different characterization techniques. Among them, NiCu exhibited the highest adsorption capacity towards Orange II and the highest activity for the production of •OH from H_2O_2 decomposition, which could be attributed to its high surface area and highly positively charged surface. However, FeCu exhibited the highest activity for the degradation of Orange II. The reason might be that FeCu has more unpaired electrons and higher redox ability, thus promoting the activation of adsorbed Orange II through the electron transfer process. By contrast, NiCu exhibited the highest activity for the removal of ciprofloxacin because ciprofloxacin was mainly degraded by •OH. Finally, the main degradation intermediates of Orange II and ciprofloxacin were determined by liquid chromatography-mass spectrometry.

1. Introduction

Removing refractory organic pollutants from water is still a challenge for environmental remediation. These pollutants can be degraded by reactive oxygen species (ROS) produced from the activation of some oxidants (Nidheesh et al., 2013; O'Shea, 2012). Heterogeneous Fenton process is considered to be an effective technology for the production of ROS. $\equiv Fe^{2+}$ and $\equiv Fe^{3+}$ can react with H_2O_2 to produce hydroxyl radical (•OH) and superoxide radicals ($\bullet O_2^-$), respectively. Meanwhile, the cycle of $\equiv Fe^{2+}/\equiv Fe^{3+}$ is formed. However, the reaction of $\equiv Fe^{3+}$ with H_2O_2 is very slow, especially at high pH values, which limits its practical application (Shi et al., 2014; Brillas et al., 2009). Therefore, some other

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multivalent metal oxides, such as cobalt, manganese, cerium and copper oxides, have also been used as Fenton-like catalysts for the activation of H_2O_2 (Ma et al., 2015; Zhang et al., 2016; Zhao et al., 2017; Gan et al., 2017). Among them, Cu-based catalysts have attracted more attention due to their higher activity at neutral pH compared to iron oxides. The reaction rates of Cu^{2+} and Cu^{+} with H_2O_2 for the generation of $\bullet O_2^-$ and •OH are both higher than that of Fe^{3+} and Fe^{2+}, and so the cycle of Cu^{2+}/Cu^{+} occurs more easily (Pham et al., 2013).

It is well known that the performance of a Fenton catalyst is dependent on its structure and surface properties. Hence, many efforts have been made to obtain effective Cu-based catalysts. Various mesoporous materials supported copper oxides have shown high Fenton-like activity, in which tiny CuO_X nanoparticles can be formed and well dispersed because of the high specific surface area and narrow pore size distribution of the support (Karthikeyan et al., 2016; Li et al., 2017; Pachamuthu et al., 2017). In recent years, the development of composite oxide catalysts have received more attention because a superior catalytic performance may be achieved due to the synergy between different components (Han et al., 2011; Wang et al., 2016; Zheng et al., 2017; Zhang et al., 2017). In particular, the coexistence of multivalent metals could accelerate the interfacial electron transfer and as well the production of active radicals from H_2O_2 decomposition. For instance, Guimaraes et al. reported that the doped Cu^{2+} significantly increased the redox ability of goethite, leading to a strong increase in Fenton-like activity (Guimaraes et al., 2009). Jin et al. found that oxygen vacancy generated in the Cu substituted Fe_3O_4@FeOOH composite should be the active sites for H_2O_2 activation (Jin et al., 2017). Yamaguchi et al. reported that Cu deposited on the surface of zero-valent iron (ZVI) suppressed the generation of OH radical, but facilitated the passivation of ZVI surface, thus promoting the formation of Fenton reagents, Fe^{2+} and H_2O_2 (Yamaguchi et al., 2018). These results indicate the potential application of transition metal composite oxides in water treatment. Therefore, the synergistic effect between Cu and other transition metals and the key parameter affecting their Fenton-like activity should be intensively studied, which could provide useful information for the rational design of Fenton catalysts.

Herein, a series of Cu-based bimetallic oxides were synthesized and investigated as a Fenton-like catalyst for the degradation of Orange II and ciprofloxacin. The structure, chemical oxidation state, surface charge property and redox ability of the catalysts were studied using different characterization techniques. The main active species in different systems were determined, and the possible catalytic mechanism for H_2O_2 activation was discussed. Finally, a possible pathway for the degradation of Orange II and ciprofloxacin was proposed according to the liquid chromatography–mass spectrometry (LC-MS) result.

2. Experimental

2.1. Catalyst preparation

Cu-based composite oxides were prepared a hydrothermal method. Since Fe-Cu composite oxide is the most widely used bimetallic oxide Fenton-like catalyst, the samples with different Fe:Cu ratios (from 5:1 to 1:5) were prepared and their Fenton-like activity for Orange II degradation was evaluated. The result showed that the sample with the Fe:Cu ratio of 1:1 exhibited the highest activity, thus the other bimetallic oxide samples were also prepared with the M:Cu ratio of 1:1 for comparison. Typically, $Cu(NO_3)_2$ and $M(NO_3)_x$ (M: Mn, Fe, Co or Ni) were dissolved with deionized water. The solution pH was adjusted to 10 with NaOH and magnetically stirred for 0.5 h. Then the mixture was transferred into an autoclave tube and heated at 120 °C for 12 h. After cooling down to room temperature, the solid product was washed with deionized water and finally dried at 60 °C overnight. The samples prepared with $Mn(NO_3)_2$, $Fe(NO_3)_3$, $Co(NO_3)_2$ and $Ni(NO_3)_2$ were designated as MnCu, FeCu, CoCu and NiCu.

2.2. Catalyst characterization

The crystal phase and surface texture of the catalysts were measured by a Bruker D8–Advance X–ray diffraction diffractometer (XRD) and a Quantachrome NOVA 4000e system. The morphology was examined by a field emission scanning electron microscope (FESEM: Hitachi S-4800). X-ray photoelectron spectroscopy (XPS) and Fourier transformation infrared (FTIR) spectra analyses were performed using a Shimadzu ESCA-3400 XPS instrument and a Nicolet iS 50 FTIR spectrometer, respectively. The point of zero charge (PZC) of the catalyst suspension was measured by a Malvern 3000 Zetasizer. Hydrogen temperature-programmed reduction (H_2-TPR) experiments were carried out on a PCA-1200 chemical adsorption instrument. After pretreating the sample with Ar at 200 °C for 1 h, the sample was reduced from 50 °C to 700 °C at a rate of 10 °C min^{-1} by a mixture of H_2 and Ar (10 vol% H_2, 30 mL min^{-1}).

2.3. Fenton-like tests

To exclude the influence of light irradiation, all the experiments were carried out in a glass vessel covered with foil. In a typical experiment, 0.05 g of catalyst was added to 100 mL of 10 mg L^{-1} ciprofloxacin or 20 mg L^{-1} Orange II aqueous solution. The resultant suspension was adjusted to pH 6 with dilute H_2SO_4 or NaOH aqueous solution and stirred for 0.5 h in order to achieve adsorption equilibrium. The Fenton-like reaction was initiated by the addition H_2O_2 (10 mM). The concentrations of Orange II and ciprofloxacin were determined by high performance liquid chromatography (HPLC, Agilent 1200) at the wavelength of 485 and 277 nm, respectively. The degradation products were analyzed by LC-MS (3200 Q TRAP, AB SCIEX) at the wavelength of 256 nm. Acetonitrile and formic acid aqueous solution were used as the mobile phase. The generated active radicals were determined by a MS-5000 electron paramagnetic resonance (EPR) spectrometer (Magnettech, Germany) using DMPO (5,5-dimethy-1-pyrroline-N-oxide) as a probe.

3. Results and discussion

3.1. Characterization of Cu-based bimetallic oxides

Fig. S1 (Supporting Information) shows the XRD patterns of the obtained samples. Only a few weak peaks can be observed, indicating their amorphous nature. The SEM images of different Cu-based bimetallic oxides are shown in Fig. S2. MnCu contains a large number of nanorods and nanoparticles. FeCu is composed of irregular nanoparticles. Some submicrospheres and nanoflakes are observed for CoCu, while nanoflakes and nanoparticles for NiCu. The result shows that the morphology of the obtained composite oxides is dependent on their composition, which could be attributed to the different growth characteristics of these metal oxides.

The surface texture of the samples was examined by nitrogen adsorption–desorption experiments. As shown in Fig. S3a, the isotherms of MnCu and CoCu can be assigned to type II, while that of FeCu and NiCu to type IV. The former implies the presence of nonporous or macroporous surfaces, while the latter is the characteristics of mesoporous structure. The steep increasing of the MnCu and CoCu isotherms at P/P_0 above 0.8 could be due to the