



Short Communication

Phenol oxidation catalyzed by a simple water-soluble copper catalyst with an imidazole salt tag

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ABSTRACT

New, simple, water-soluble copper catalysts with an imidazole salt tag [Cu-Imace-H][X] ($X^- = \text{Cl}^-$, Br^- , HSO_4^- , NO_3^- , and BF_4^-) were synthesized via an organic solvent-free method. They were characterized by ^1H NMR, ^{13}C NMR, IR, UV–Vis, ESR, ESI-MS, elemental analysis, and melting point measurements. These catalysts are effective for phenol oxidation to dihydroxy derivatives in water with H_2O_2 as oxidant. The anion evidently affects the appearance and electronic structure of the catalysts, as well as their catalytic reactivity. Both the phenol oxidation and catalyst syntheses were organic solvent-free to ensure a green process.

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1. Introduction

Oxidation is one of the most important reactions in the current chemical industry. Performing oxidation reaction in water has two clear advantages: (1) it reduces the use of organic solvents, which is one of the aims of green chemistry and green chemical industry; and (2) oxidation reactions synchronously using $\text{O}_2/\text{H}_2\text{O}_2$ and vaporific organic solvents have a high explosion risk [1,2].

Phenol oxidation is an important method of producing catechol and hydroquinone which are widely used as flavoring agents, perfumes, antioxidants, photographic developers, and materials of medication. Phenol has a higher solubility in water when the temperature is above 65°C . Therefore, phenol oxidation is ideally performed in water. Both heterogeneous and homogeneous catalysts have been used in phenol oxidation [3–28]. Although heterogeneous catalysts cannot be dissolved in water, they can absorb water and organic molecules into their pores. Most of these reported heterogeneous catalytic processes about phenol oxidation can be well performed in water [3–18].

Besides, organometallic compounds encapsulated in zeolite or supported by polymer have also been used [19–22]. Comparing with the heterogeneous catalysts, the homogeneous catalysts are easier to be synthesized. Some homogeneous catalysis processes of phenol oxidation have been reported [23–28]. However, because of the insolubility of the catalysts in water, most of these processes have to use an organic solvent such as CNCH_3 [19–23].

Organometallic copper compound, as a big family in the field of catalysis, has received much attention. Most of these reported Cu-complexes have bad solubility in water, which makes it difficult to use them in aqueous phase catalysis [29]. As a continuation of the work to develop water-soluble catalyst for oxidation reactions [30,31], herein, we report new and simple water-soluble copper catalysts with an imidazole salt tag [Cu-Imace-H][X] ($X^- = \text{Cl}^-$, Br^- , HSO_4^- , NO_3^- , and BF_4^-) and their application in phenol oxidation in water.

2. Experiment

2.1. Catalyst preparation and characterization

[Cu-Imace-H][X] catalysts were prepared in two steps (Fig. 1). The preparation of [Cu-Imace-H][Cl] was taken as an example. Other [Cu-Imace-H][X] ($X^- = \text{Br}^-$, HSO_4^- , NO_3^- , and BF_4^-) catalysts were synthesized using a similar method.

First, 12.6 g (0.01 mol) 1-imidazoleacetic acid (Imace) was reacted with 11.0 g (0.11 mol) hydrochloric acid (36%) in 60 ml water at 50°C for 3 h. The reaction mixture was evaporated under reduced pressure at 80°C , and a white powder was obtained. Water was used to recrystallize the powder, and pure [Imace-H][Cl] was obtained. Subsequently, 14.6 g (0.090 mol) [Imace-H][Cl] was reacted with 8.9 g (0.045 mol) $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in 100 ml water at 100°C . The generated acetic acid was removed using water vapor. New amount of water (50 ml) was continuously added into the reaction system until the reaction was completed. The reaction mixture was then evaporated under reduced pressure at 80°C , and a light-green powder was obtained. Water was used to recrystallize the powder to obtain pure [Cu-Imace-H][Cl] (yield: 88.4%).

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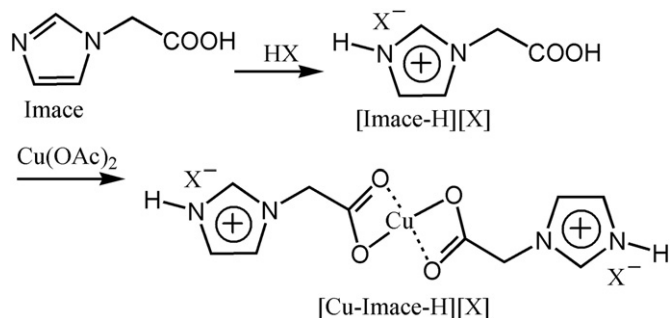


Fig. 1. Synthesis method of [Cu-Imace-H][X] ($X^- = \text{Cl}^-, \text{Br}^-, \text{HSO}_4^-, \text{NO}_3^-, \text{and } \text{BF}_4^-$).

The yields of [Cu-Imace-H][Br], [Cu-Imace-H][HSO₄], [Cu-Imace-H][NO₃], and [Cu-Imace-H][BF₄] were 84.7%, 76.5%, 78.9%, and 91.3%, respectively. These catalysts were characterized using nuclear magnetic resonance (¹H NMR and ¹³C NMR) (Bruker, DRX500), infrared spectroscopy (IR), ultraviolet-visible light spectroscopy (UV-Vis), electron spin resonance (ESR) (Bruker, EMX 10/12), electrospray ionization mass spectrometry (ESI-MS), elemental analysis, and melting point measurements. These characterization methods are convictive for homogeneous catalysts [23–29].

[Imace-H][Cl]: ¹H NMR (D₂O) δ (ppm) 5.03 (2 H, s, CH₂), 7.42 (2 H, s, N-CH), 8.70 (H, s, CH-N-CH). ¹³C NMR (D₂O) δ (ppm) 49.6 (–CH₂–), 117.4 (N-CH), 122.9 (N-CH), 135.8 (N-CH-N), 169.9 (–COOH). Melting point: 206.6–207.6 °C. [Cu-Imace-H][Cl]: IR (ν/cm^{–1}) 3122.7, 2978.9, 1639.8, 1381.6, 1289.9, 1089.7, 773.0, 697.9, 623.3, 464.9. UV-vis (Acetic acid) λ_{max} (nm) 253.5. C₁₀H₁₂Cl₂N₄O₄Cu: Calc. C 31.06, H 3.13, N 14.49; Found C 30.04, H 2.90, N 15.07. MS (ESI) m/z = 157.25 ([Cu-Imace-H]²⁺).

[Imace-H][NO₃]: ¹H NMR (D₂O) δ (ppm) 5.16 (2 H, s, CH₂), 7.43 (2 H, s, N-CH), 8.71 (H, s, CH-N-CH). ¹³C NMR (D₂O) δ (ppm) 49.7 (–CH₂–), 119.5 (N-CH), 123.0 (N-CH), 135.9 (N-CH-N), 169.8 (–COOH). Melting point: 122.3–123.4 °C. [Cu-Imace-H][NO₃]: IR (ν/cm^{–1}) 3162.2, 2978.1, 1632.6, 1538.1, 1383.7, 1306.3, 1099.8, 824.8, 764.6, 696.1, 618.7. UV-vis (Acetic acid) λ_{max} (nm) 258.0. C₁₀H₁₂N₆O₁₀Cu: Calc. C 27.04, H 2.70, N 18.93; Found C 27.99, H 3.02, N 19.30. MS (ESI) m/z = 157.25 ([Cu-Imace-H]²⁺).

[Imace-H][Br]: ¹H NMR (D₂O) δ (ppm) 5.15 (2 H, s, CH₂), 7.39 (2 H, s, N-CH), 8.68 (H, s, CH-N-CH). ¹³C NMR (D₂O) δ (ppm) 49.8 (–CH₂–), 119.4 (N-CH), 122.9 (N-CH), 135.8 (N-CH-N), 170.2 (–COOH). Melting point: 190.9–192.1 °C. [Cu-Imace-H][Br]: IR (ν/cm^{–1}) 3152.8, 2980.3, 1620.6, 1390.6, 1301.9, 1089.2, 779.4, 699.6, 611.0. UV-vis (Acetic acid) λ_{max} (nm) 250.2. MS (ESI) m/z = 157.25 ([Cu-Imace-H]²⁺).

[Imace-H][HSO₄]: ¹H NMR (D₂O) δ (ppm) 4.97 (2 H, s, CH₂), 7.41 (2 H, s, N-CH), 8.72 (H, s, CH-N-CH). ¹³C NMR (D₂O) δ (ppm) 49.6 (–CH₂–), 119.3 (N-CH), 122.9 (N-CH), 135.6 (N-CH-N), 170.8 (–COOH). Melting point: 193.4–193.6 °C. [Cu-Imace-H][HSO₄]: IR (ν/cm^{–1}) 3153.2, 2979.9, 2936.7, 1636.0, 1543.2, 1388.3, 1303.2, 1225.8, 1094.1, 869.5,



Fig. 2. The colors of [Cu-Imace-H][X]. From left to right: $X^- = \text{Cl}^-, \text{Br}^-, \text{HSO}_4^-, \text{NO}_3^-, \text{and } \text{BF}_4^-$.

745.9, 691.6, 598.7, 521.3. UV-vis (Acetic acid) λ_{max} (nm) 254.6. MS (ESI) m/z = 157.25 ([Cu-Imace-H]²⁺).

[Imace-H][BF₄]: ¹H NMR (D₂O) δ (ppm) 5.13 (2 H, s, CH₂), 7.43 (2 H, s, N-CH), 8.71 (H, s, CH-N-CH). ¹³C NMR (D₂O) δ (ppm) 49.6 (–CH₂–), 119.4 (N-CH), 123.0 (N-CH), 135.9 (N-CH-N), 169.9 (–COOH). Melting point: 168.6–170.6 °C. [Cu-Imace-H][BF₄]: IR (ν/cm^{–1}) 3150.1, 2999.4, 1618.5, 1575.7, 1404.3, 1318.7, 1108.5, 1073.5, 1034.5, 773.6, 703.5, 652.8, 586.7, 520.7. UV-vis (Acetic acid) λ_{max} (nm) 253.3. MS (ESI) m/z = 157.25 ([Cu-Imace-H]²⁺).

2.2. Phenol oxidation experiments

The reaction was performed in a four-necked round bottom reactor (The four necks are used for stirring, refluxing, measuring temperature, and adding H₂O₂, respectively). The following is a typical oxidation process: 9.4 g (0.1 mol) phenol, 9.4 g water, and 0.0005 mol catalyst were mixed in the reactor at a reaction temperature of 70 °C. 0.1 mol 30% H₂O₂ was added into the reaction system at a rate of 0.1 ml/min using a pump. Samples of the reaction mixture were regularly collected and analyzed to monitor the reaction via gas chromatography according to these previously reported methods [18,19,24,26].

3. Results and discussion

3.1. Characteristics of the catalysts

The ¹³C NMR spectroscopy clearly shows all of the carbon in the target structure, and these chemical shifts are typical for carbon in –CH₂–, imidazole and –COOH. For the ¹H NMR, all of the protons were correctly presented except that the –COOH proton was not observed. This proton has been exchanged by D₂O. A peak with m/z = 157.25 was obtained for all of the catalysts in the ESI-MS. This peak corresponds to the [Cu-Imace-H]²⁺. Further evidence comes from the elemental analysis, which give satisfying match between calculated and experimental data. The vibration of C–H, N–H, C=O and C–N were clearly shown in the IR spectroscopy. Though several solvents (including H₂O, methanol, acetic acid and chloroform) were used for the UV-vis mensuration, only one band was observed (ranging from 250.2 to 258.0 nm for different catalysts), which corresponds to the n → π* transition. The ESR spectroscopies show that one copper coordinates with four oxygens in the catalysts. All of the characterizations (¹H NMR, ¹³C NMR, IR, UV-Vis, ESR, ESI-MS, and elemental analysis) proved that the catalysts have been synthesized correctly.

Five catalysts with different anions were synthesized in this paper. One interesting character is that their colours are completely different from one another. The colours of the catalysts with Cl[–], Br[–], HSO₄[–], NO₃[–], and BF₄[–] as anions are light-green, deep-green, purple, light-blue, and light-purple, respectively (Fig. 2). The ESR, IR, UV-Vis, and NMR results of these catalysts also differ from one another (Fig. 3 and Table 1).

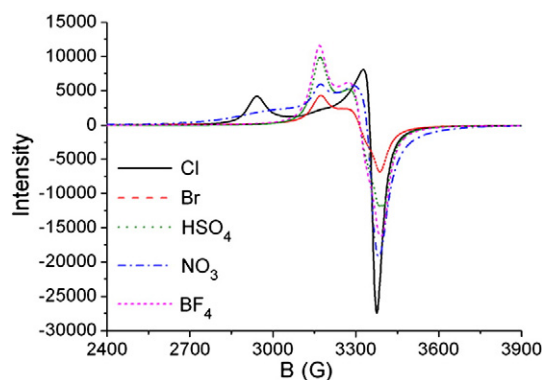


Fig. 3. The ESR spectroscopy of [Cu-Imace-H][X].

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