



Short Communication

Copper-cationic salphen catalysts for the oxidation of cyclohexene by oxygen

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ABSTRACT

The modified copper-cationic salphen catalysts were synthesized and used in the allylic oxidation of cyclohexene to 2-cyclohexen-1-ol and 2-cyclohexen-1-one with oxygen under mild conditions. Compared with their unmodified counterpart, the catalytic activities of modified catalysts are improved. The type of counteranion could affect the reactivity of catalyst, which offers an opportunity to improve the catalysts via changing counteranions to optimize the selectivity. The cation–anion interaction can be adjusted by different solvents, which in turn influences the catalyst reactivity. Furthermore, these novel catalysts can be reused without sacrificing the activity.

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1. Introduction

Metal-salen complexes are an important class of coordination compounds, and it has long been recognized that the catalysts can be modified with various substituent groups on ligands [1–7]. However, they suffer some problems in homogeneous medium, including difficulty in separation from the reaction mixture and recycling. Immobilization of the salen catalysts on some supports to create heterogeneous catalysts was used to overcome these difficulties, however this method suffers from different disadvantages, such as lower accessibility of substrates, poor activity and also leaching of active species [8–18].

To solve these challenges, ionic compound was developed as an efficient strategy owing to their intriguing physical and chemical properties [19–24]. Modified ionic catalysts have obtained common advantages of facilitating product isolation, reusing of the catalysts and in some cases accelerating the reactions [25,26]. However, there are a few reports on the effect of the counteranion on the reactivity of these supported catalysts [17,26].

Herein, we designed and synthesized copper-cationic salphen, whose catalytic activity could be improved using various counteranions, Cu-[cationic salphen][X[−]]₂ (Scheme 1). The most appealing features of the catalysts were that the anion interacted with the cation, thus the cation–anion interaction could easily deliver to the metal center. The

catalyst reactivity could be improved by altering the type of counteranion in ionic salts or changing the strength of the interaction between cation and anion.

2. Experimental

2.1. Materials and methods

All the chemicals were purchased from MERCK Chemical Co. *O*-phenylene diamine was sublimated for further purification. 2,3-Diaminophenazine was prepared and purified according to the previously reported method [27,28]. Other solvents and chemicals were purified by common procedures.

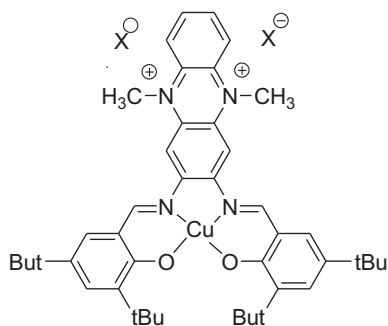
¹H NMR (500 MHz) spectra were obtained in deuterated solvents on a Bruker Avance 500 instrument (Bruker, Rheinstetten, Germany), UV–Vis absorption spectra were obtained in DMSO (ca. 910–5 M) on a JASCO-570 UV–Visible spectrometer and FT-IR spectra were obtained as KBr pellets with a 680 plus-JASCO. Elemental analyses were performed with a CHNS-932, Leco. The progress of reaction was monitored and controlled by Shimadzu gas chromatograph (model 14A) equipped with a wide bore OV-17 (60 m) capillary column and an FID detector. The structure of products and by-products was further identified using HP6890 GC/MS spectrometer by comparing the retention times and the fragmentation patterns with authentic samples.

2.2. Preparation of the Cu-[cationic salphen][I[−]]₂

The cationic Cu-[cationic salphen][I[−]]₂ was prepared and purified according to the procedure already published in the literature [28];

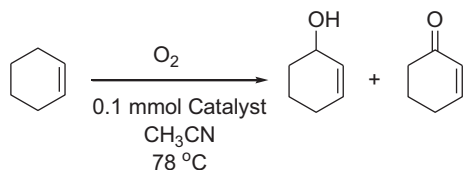
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Scheme 1. Structure of Cu-[cationic salphen][X⁻]₂.

2,3-Diaminophenazine (0.21 g, 1 mmol), 3,5-di t-butyl-2-hydroxy benzaldehyde (0.468 g, 2 mmol), and Cu(OAc)₂·3H₂O (0.23 g, 1 mmol) in absolute ethanol were stirred under reflux condition for 12 h. Then, the excess amount of methyl iodide was added and refluxed for 7 days. A brown solid was obtained by removal of the unreacted methyl iodide under reduced pressure. Yield (%) = 96; FT-IR (KBr): ν = 3415, 2919, 2856, 1629, 1462, 1438, 1230, 1113, 743 cm⁻¹; Anal. Calcd. (%) for C₄₄H₅₄CuI₂N₄O₂: C, 53.47; H, 5.51; N, 5.67; Found: C, 52.87; H, 5.36; N, 5.39. Atomic Absorption Spectroscopy: Cu-[cationic salphen][I⁻]₂: Found: Cu, 6.12%.



Scheme 2. The oxidation of cyclohexene.

2.3. Synthesis of Cu-[cationic salphen][X⁻]₂

Cu-[cationic salphen][X⁻]₂: AgX (X = NO₃, Br, CF₃COO) or NH₄PF₆ (2 mmol) was added to the Cu-[cationic salphen][I⁻]₂ (1 mmol) in acetonitrile (50 ml), and then the mixture was stirred away from light at room temperature for 3 h. The resulted mixture was filtered and the filtrate was evaporated under reduced pressure at 60 °C, and the obtained solid was dried in vacuum. The Cu-[cationic salphen][X⁻]₂ was prepared.

Cu-[cationic salphen][NO₃⁻]₂: Yield: 95%. Atomic Absorption Spectroscopy: Cu-[cationic salphen][NO₃⁻]₂: Found: Cu, 8.38%. FT-IR (KBr): 3423, 2925, 2857, 1725, 1627, 1461, 1383, 1274, 1122, 408 cm⁻¹.

Cu-[cationic salphen][Br⁻]₂: Yield: 91%. Atomic Absorption Spectroscopy: Cu-[cationic salphen][Br⁻]₂: Found: Cu, 6.85%. FT-IR (KBr): 3430, 2923, 2862, 1624, 1595, 1463, 1380, 1308, 1267, 1126, 1089, 1033, 781, 698, 535, 457 cm⁻¹.

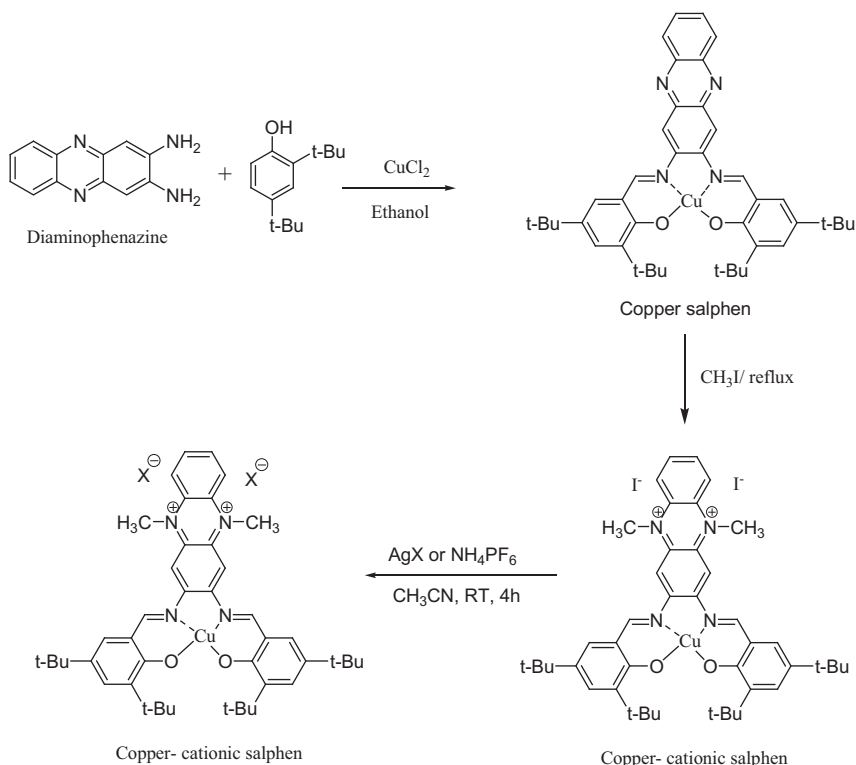
Cu-[cationic salphen][PF₆⁻]₂: Yield: 88%. Atomic Absorption Spectroscopy: Cu-[cationic salphen][PF₆⁻]₂: Found: Cu, 6.03%. FT-IR (KBr): 3392, 2933, 2871, 1662, 1434, 1390, 1171, 1066, 945, 856, 728, 554, 418 cm⁻¹.

Cu-[cationic salphen][CF₃COO⁻]₂: Yield: 79%. FT-IR (KBr): 3442, 2929, 2868, 1687, 1629, 1476, 1430, 1288, 1201, 1127, 841, 795, 727, 455 cm⁻¹.

2.4. Cyclohexene oxidation catalyzed by Cu-[cationic salphen][X⁻]₂

The Cu-[cationic salphen][X⁻]₂ was used as catalysts for the allylic oxidation of cyclohexene.

A 25 ml three-necked round-bottomed flask was charged with 10 mmol cyclohexene, 10 ml CH₃CN, and 0.1 mmol Cu-[cationic salphen][X⁻]₂. The resulting mixture was performed at 78 °C in a water bath with fast stirring. The oxygen was flowing into the reactor, after completion of the reaction, the solvent was removed by evaporation under reduced pressure at 60 °C and the products were collected by evaporation under reduced pressure at 100 °C. Subsequently, the



Scheme 3. Synthesis of Cu-[cationic salphen][X⁻]₂.

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