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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.

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.

^{1}H 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 bone 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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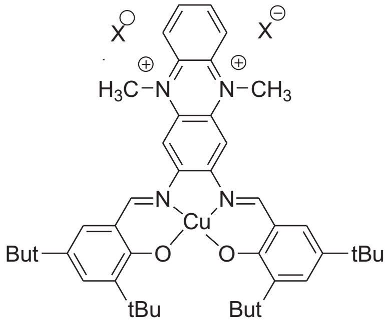
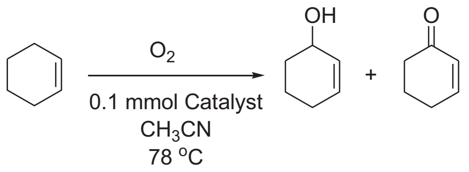


Scheme 1. Structure of Cu-[cationic salphen][X^-]$_2$.

2,3-Diaminophenazine (0.21 g, 1 mmol), 3,5-di t-butyl-2-hydroxy benzaldehyde (0.468 g, 2 mmol), and $Cu(OAc)_2 \cdot 3H_2O$ (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): m = 3415, 2919, 2856, 1629, 1462, 1438, 1230, 1113, 743 cm^{-1}; Anal. Calcd. (%) for $C_{44}H_{54}CuI_2N_4O_2$: 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 = NO_3, Br, CF_3COO) or NH_4PF_6 (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][NO_3^-]$_2$: Yield: 95%. Atomic Absorption Spectroscopy: Cu-[cationic salphen][NO_3^-]$_2$: 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, 28621624, 1595, 1463, 1380, 1308, 1267, 1126, 1089, 1033,781, 698, 535, 457 cm^{-1}.

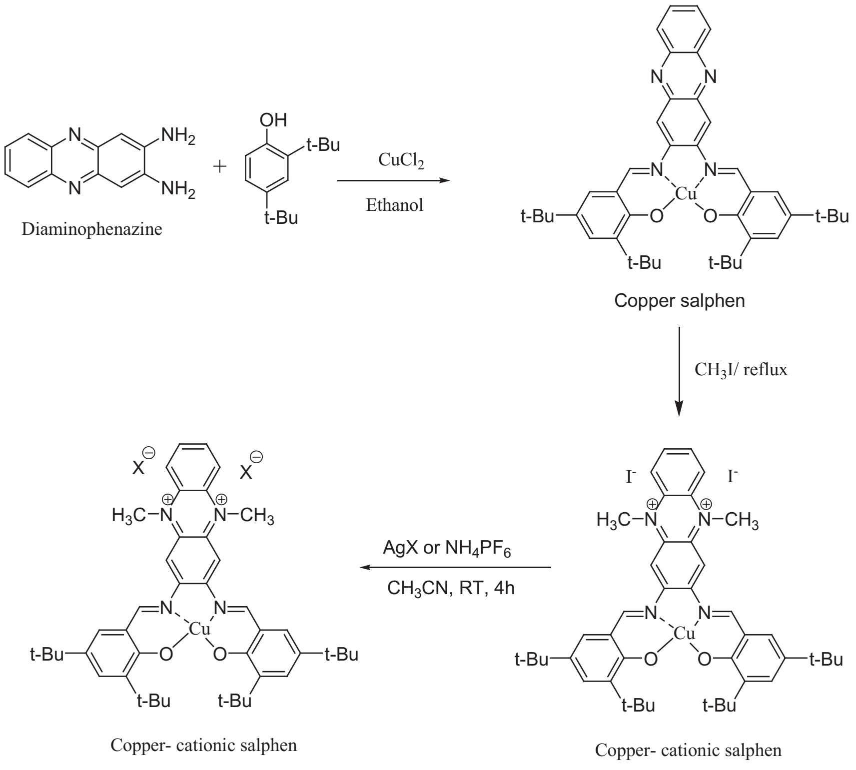
Cu-[cationic salphen][PF_6^-]$_2$: Yield: 88%. Atomic Absorption Spectroscopy: Cu-[cationic salphen][PF_6^-]$_2$: Found: Cu, 6.03%. FT-IR(KBr): 3392, 2933, 2871, 1662, 1434, 1390, 1171, 1066, 945, 856, 728, 554, 418 cm^{-1}.

Cu-[cationic salphen][CF_3COO^-]$_2$: 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 CH_3CN, 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^-]$_2$.

Table 1
The results of the oxidation of cyclohexene with Cu-[cationic salphen][X^-]$_2$ and copper salphen.

Entry	X	Time (h)	Conversion (%)	Selectivity (%)	
				-ol	-one
1	Copper salphen	24	23	65.3	32.6
2	Br^-	16	100	23.9	64.1
3	NO_3^-	16	100	26.5	59.2
4	CF_3COO^-	16	100	28.7	56.6
5	PF_6^-	16	100	39.4	48.7
6	I^-	16	100	24.1	63.9

The oxidation of cyclohexene was performed with cyclohexene (6 mmol), catalyst (1% molar percentage) in 5 ml CH_3CN at 78 °C.

catalyst was used without further purification. The progress of the reaction was followed by GC (with benzyl ethanoate as the internal standard). The products were analyzed by GC–MS. Besides, a series of comparative experiments with different catalysts and different conditions were carried out.

3. Results and discussion

The procedure for catalyst preparation is depicted in Scheme 2. The Cu-[cationic salphen][X^-]$_2$ was prepared by the reaction of Copper salphen in the presence of excess methyl iodide as a reagent and a solvent under reflux. The two CH_3–N^+ groups were formed in the salphen ligand and neutralized by two iodide anions. To study the effect of counteranions on the reactivity of these catalysts, the iodide anions were exchange with different counteranions (Scheme 3). Altering the counteranion only needs an ion change process which occurred in a high yield (79–95%).

3.1. The effect of the counteranion on the reactivity of the catalysts

The Cu-[cationic salphen][X^-]$_2$ was found to be an effective and selective catalyst for oxidation of cyclohexene to the corresponding 2-cyclohexen-1-ol and 2-cyclohexen-1-one with oxygen as the oxidant under mild conditions (Table 1). The conversion was measured by GC method. Employing this system, cyclohexene was converted to 2-cyclohexen-1-ol and 2-cyclohexen-1-one (depending on the reaction condition, time and temperature) in high yields (up to 100% conversion) and selectivity.

The effect of the counteranion in ionic compound shows the influence on the selectivity and the conversion of reaction, although non-cationic salphen complex is noticeably less active in comparison to Cu-[cationic salphen][X^-]$_2$. It was interesting to find that the type of counteranion could affect the catalytic activity (Entry 2–6). Different counteranions in ionic Cu-[cationic salphen][X^-]$_2$ can change the electric structure of the active center of the catalysts, which in turn adjusts the properties of the catalysts via altering the type of counteranion. Activities of catalysts with different counteranions followed the order in a trend expected of their nucleophilicity in CH_3CN.

Table 2
The results of the oxidation of cyclohexene in different solvents over the Cu-[cationic salphen][Br^-]$_2$ and Cu-[cationic salphen][PF_6^-]$_2$.

Entry	Catalysts	Solvent	Conversion (%)	Selectivity (%)	
				-ol	-one
1	Cu-[cationic salphen][PF_6^-]$_2$	CH_3CN	100	39.4	48.9
	Cu-[cationic salphen][Br^-]$_2$		45	25.1	59.3
2	Cu-[cationic salphen][PF_6^-]$_2$	DMF	100	44.1	41.3
	Cu-[cationic salphen][Br^-]$_2$		49	26.9	61.1
3	Cu-[cationic salphen][PF_6^-]$_2$	CH_3OH	94	43.8	40.7
	Cu-[cationic salphen][Br^-]$_2$		67	26.4	62.9
4	Cu-[cationic salphen][PF_6^-]$_2$	CH_3COOH	68	35.9	52.7
	Cu-[cationic salphen][Br^-]$_2$		37	33.9	57.2
5	Cu-[cationic salphen][PF_6^-]$_2$	CH_2Cl_2	31	31.8	48.7
	Cu-[cationic salphen][Br^-]$_2$		25	30.1	53.8

The oxidation of cyclohexene was performed with cyclohexene (6 mmol), catalyst (1% molar percentage) in 5 ml of solvent at 78 °C, 16 h.

Table 3
The recycling studies of Cu-[cationic salphen][PF6—]2 in the oxidation of cyclohexene.

Entry	Run times	Conversion (%)	Selectivity (%)	
			-ol	-one
1	Fresh	100	39.4	48.9
2	2nd	100	41.2	45.1
3	3rd	98	41.9	44.2
4	4th	97	42.8	42.7
5	5th	89	44.6	37.3

The oxidation of cyclohexene was performed with cyclohexene (6 mmol), catalyst (1% molar percentage) in 5 ml CH_3CN at 78 °C, 16 h.

Different solvents were employed on the oxidation of cyclohexene (Table 2) and due to the better solubility of the catalyst, the polar solvent was more suitable for this reaction. The polarity of solvent had influence on the cation and anion separation and the direct interaction between anion and cation made the reactivity of the catalyst different from each other. Different counteranions in ionic compounds can change the electric structure of the active center of the catalysts, which in turn adjusts the properties of the catalysts via altering the type of counteranion.

Finally, recyclability of the catalyst in the oxidation reaction was also examined under optimized conditions. As shown in Table 3, the recovery was accomplished in five sequential reaction runs with only a slight loss of catalytic activity (less than 3% for 4 run) and selectivity.

4. Conclusions

Some new types of Cu-[cationic salphen][X^-]$_2$ complexes with two cationic sites, as an excellent active catalyst on the allylic oxidation of cyclohexene were synthesized. These easily reconstructed complexes show better conversion compared to non-cationic complex. The types of counteranion could affect the catalytic activity of the catalysts, and also the reactivity and selectivity of catalysts change by changing the solvent polarity due to the change of the cation–anion interaction. Moreover, the catalyst could be used at least four times without significant loss of catalytic activity and selectivity.

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