



## Copper-salen catalysts modified by ionic compounds for the oxidation of cyclohexene by oxygen

Xiao Yun, Xingbang Hu, Zhiyuan Jin, Jinghui Hu, Chao Yan, Jia Yao, Haoran Li\*

Department of Chemistry, Zhejiang University, ZheDa Road, Hangzhou 310027, PR China

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### ABSTRACT

Copper-salen catalysts modified by ionic compounds were synthesized and used in the allylic oxidation of cyclohexene to 2-cyclohexen-1-ol and 2-cyclohexen-1-one with oxygen as the oxidant under mild conditions. Compared with their unmodified counterpart, the catalytic activities of these modified catalysts are improved, thereby facilitating the development of highly efficient catalysts. The type of counteranion could affect the reactivity of catalyst, which offers an opportunity to improve the catalysts via changing counteranions. The cation–anion interaction can be adjusted by different solvents, which in turn influencing the catalyst reactivity. Furthermore, these novel catalysts can be reused without sacrificing the activity.

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### 1. Introduction

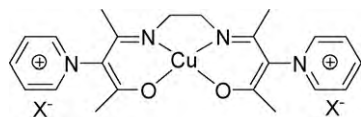
Metal-salen complexes have attracted the interest of chemists for more than 80 years [1]. Developing high effective salen catalysts has always been a challenging research. It has been long recognized that the catalysts can be modified with various substituent groups on ligands [2–5]. However, these salen catalysts suffer some problems in homogeneous medium, including difficulty in separation from the reaction mixture and recycling. One approach for overcoming these difficulties is to immobilize the salen catalysts on some supports to create heterogeneous catalysts, such as immobilization of salen catalysts using inorganic supports [6–9], mesoporous materials [10–13], and organic polymer [14–16]. Unfortunately, comparing with the homogeneous salen catalysts, the heterogeneous catalysts often suffer from various disadvantages, such as poor activity, low accessibility of substrates, and leaching of the active species into the reaction medium. Therefore, it is challenging to develop an efficient strategy for catalyst recovery which can keep the reactivity of the catalyst or even improve it.

Ionic compounds have attracted attention in several scientific disciplines owing to their intriguing physical and chemical properties [17–19]. The properties of ionic salts can be tuned by combining different cations and anions. More recently, ionic compounds have been recognized as potential media for the immo-

bilization of catalysts. Jacobsen catalysts [20–23] and some other catalysts [24–29] have been modified by ionic compounds. These catalysts have common advantages, facilitating product isolation and offering an opportunity to reuse the catalysts. In addition, some of them have been reported to obtain the advantage of accelerating reactions [30,31]. Although there are extensive applications of catalysts supported by ionic compounds, the effect of the counteranion on the reactivity of these supported catalysts has been received little attention. As far as we know, there are a few papers concerned on the catalysts supported by ionic compounds with different anions. Dyson synthesized  $[\text{PdCl}_2(\text{C}_3\text{CNpy})_2][\text{X}^-]$  ( $\text{X}^- = \text{Cl}^-, \text{PF}_6^-, \text{BF}_4^-, \text{PdCl}_4^{2-}, \text{N}(\text{SO}_2\text{CF}_3)_2^-$ ) with different anions. However, no significant differences on catalytic activity with different anions were found in Suzuki coupling reaction [32]. Designing a kind of ionic compound supported catalyst, whose catalytic activity could be improved using various cation–anion, would greatly simplify the process of modifying catalyst.

Herein, we designed and synthesized copper-salen catalysts modified by ionic compounds,  $\text{M}[\text{Salen-Py}][\text{X}^-]_2$  (Scheme 1). The most appealing features of the catalysts were that the cation of ionic salts connected with the metal center by conjugated double bond and the anion interacted with the cation through hydrogen bond, 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. The catalysts could expediently be reused.

\* Corresponding author. Tel.: +86 571 8795 2424; fax: +86 571 8795 1895.  
E-mail address: [lihr@zju.edu.cn](mailto:lihr@zju.edu.cn) (H. Li).



**Scheme 1.** Structure of Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> (X = Br, NO<sub>3</sub>, BF<sub>4</sub>, CF<sub>3</sub>COO, PF<sub>6</sub>).

## 2. Experimental

### 2.1. Materials and methods

The cyclohexene and *N*-bromosuccinimide (NBS) were obtained from Acros organics. Other reagents and solvents were of pure analytical grade materials purchased from commercial sources and used without further purification unless otherwise indicated.

The NMR spectra were detected by Bruker ARX 500 NMR spectrometer, and TMS as the internal standard. FT-IR spectra were recorded on a Bruker APEX-III spectrometer using KBr pellets in 400–4000 cm<sup>-1</sup> region. The ultraviolet–visible light (UV–vis) spectra were recorded on a UV–vis SPECORD 200 spectrophotometer. Electron spin resonance (ESR) signals were recorded at ambient temperature (120 K) with a Bruker ESR A300 spectrometer. Catalyst stability was recorded on Perkin Elmer Pyris 6 thermal-gravity (TG) analysis equipment. The progress of reaction was monitored and controlled by Shang Feng GC-112A gas chromatograph fitted with a SE-30 column (50 m, 0.025 μm diameters) and a flame ionization detector. The structure of products and by-products was further identified using HP6890 GC/MS spectrometer by comparing retention times and fragmentation patterns with authentic samples.

### 2.2. Preparation of the M-[Salen-Py][X<sup>-</sup>]<sub>2</sub>

The preparation of the M-[Salen-Py-IL][X<sup>-</sup>]<sub>2</sub> is outlined in Scheme 2.

#### 2.2.1. Synthesis of acetylaceton–ethylenediimine (1)

The acetylaceton–ethylenediimine (**1**) was synthesized according to the modified procedure. Ethylenediimine (0.45 mol) dissolved in acetyl acetone (100 ml) was heated to 105 °C under stirring for 24 h, dewatering via water-separator. Upon filtration, the precipitate was collected and recrystallized from chloroform–pentane (1:1 (V/V)), dried in vacuo to get a pale-yellow powder of **1**. Yield: 59%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ ppm 10.90 (s, 2H), 5.01 (s, 2H), 3.43–3.44 (t, 4H, *J* = 3.19), 2.01 (s, 6H), 1.92 (s, 6H). Compound **1**: Calc. for C<sub>12</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 64.26; H, 8.99; N, 12.49. Found: C, 64.30; H, 8.98; N, 12.39. FT-IR (KBr): 3449, 2949, 1609, 1577, 1520, 1451, 1434, 1372, 1353, 1287, 1220, 1143, 1087, 1022, 979, 940, 851, 759, 739, 641, 521 cm<sup>-1</sup>. Melting point: 111.0–111.5 °C.

#### 2.2.2. Synthesis of H<sub>2</sub>(3-Br-acacen) (2)

The above-obtained **1** (0.06 mol) dissolved in 50 ml acetonitrile, followed by the addition of *N*-bromosuccinimide (0.12 mol) with acetonitrile (50 ml) at 0 °C. The mixture was stirred for another 1 h at 0 °C. The resulted solid was filtered and recrystallized from chloroform–ethanol (1:1 (V/V)), dried in vacuo, and **2** was prepared. Yields: 47%. <sup>1</sup>H NMR (DMSO, 500 MHz): δ ppm 11.62 (s, 2H), 3.49–3.51 (t, 4H, *J* = 2.98), 2.37 (s, 6H), 2.22 (s, 6H). Compound **2**: Calc. for C<sub>12</sub>H<sub>18</sub>BrN<sub>2</sub>O<sub>2</sub>: C, 37.72; H, 4.75; N, 7.33. Found: C, 37.59; H, 3.58; N, 7.17. FT-IR (KBr): 3449, 2941, 1778, 1698, 1577, 1465, 1357, 1265, 1242, 1184, 1102, 1024, 986, 958, 880, 813, 757, 687, 635, 575 cm<sup>-1</sup>. Melting point: 140.9–141.7 °C.

#### 2.2.3. Synthesis of [Salen-Py][Br<sup>-</sup>]<sub>2</sub> (3)

The above-obtained **2** (0.04 mol) dissolved in pyridine (100 ml) was stirred under reflux for 3 h. On filtration, precipitate was collected and recrystallized from acetonitrile. The obtained solid was dried in vacuo to give a brown powder of **3**. Yields: 64%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ ppm 11.36 (s, 2H), 9.13–9.14 (d, 4H, *J* = 5.7); 8.81–8.84 (t, 2H, *J* = 7.80); 8.31–8.34 (t, 4H, *J* = 7.05) 3.67–3.68 (t, 4H, *J* = 2.85), 1.78 (s, 6H), 1.72 (s, 6H). Compound **3**: Calc. for C<sub>22</sub>H<sub>28</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>2</sub>: C, 48.91; H, 5.22; N, 10.39. Found: C, 44.99; H, 5.41; N, 9.49. FT-IR (KBr): 3449, 3041, 1626, 1611, 1556, 1469, 1431, 1365, 1336, 1288, 1211, 1128, 1069, 1024, 971, 878, 810, 784, 690, 574, 496 cm<sup>-1</sup>. Melting point: 162.6–164.8 °C.

#### 2.2.4. Synthesis of M-[Salen-Py][Br<sup>-</sup>]<sub>2</sub> (4)

Cu-[Salen-Py][Br<sup>-</sup>]<sub>2</sub>: A solution of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.03 mol) in ethanol (50 ml) was added dropwise to 50 ml ethanol solution containing 0.03 mol **3**, and then the mixture was stirred under reflux for another 3 h. The resulting slurry was cooled to 5 °C for 2 h, filtered and the precipitate recrystallized from acetonitrile, dried in vacuo, Cu-[Salen-Py][Br<sup>-</sup>]<sub>2</sub> was prepared. Yields: 64%. Cu-[Salen-Py][Br<sup>-</sup>]<sub>2</sub>: Calc. for C<sub>22</sub>H<sub>28</sub>Br<sub>2</sub>CuN<sub>4</sub>O<sub>2</sub>: C, 43.91; H, 4.35; N, 9.31. Found: C, 44.41; H, 5.51; N, 9.38. ESI-MS, *m/z* = 220.6 [(Cu-[Salen-Py][Br<sup>-</sup>]<sub>2</sub>-2Br)/2]<sup>+</sup>. FT-IR (KBr): 3410, 3030, 1622, 1594, 1467, 1429, 1351, 1303, 1264, 1221, 1158, 1105, 1080, 1050, 1019, 961, 788, 732, 695, 663, 634, 453 cm<sup>-1</sup>.

#### 2.2.5. Synthesis of Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub>

Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub>: AgX (X = NO<sub>3</sub>, BF<sub>4</sub>, CF<sub>3</sub>COO) or NH<sub>4</sub>PF<sub>6</sub> (2 mmol) was added to the Cu-[Salen-Py][Br<sup>-</sup>]<sub>2</sub> (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 vacuo. Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> was prepared.

Cu-[Salen-Py][NO<sub>3</sub><sup>-</sup>]<sub>2</sub>: Yield: 91%. Atomic Absorption Spectroscopy: Cu-[Salen-Py][NO<sub>3</sub>]<sub>2</sub>·5H<sub>2</sub>O: Calc. for C<sub>22</sub>H<sub>36</sub>CuN<sub>6</sub>O<sub>13</sub>: Cu, 9.69%. Found: Cu, 9.69%. ESI-MS, *m/z* = 503.2 (Cu-[Salen-Py][NO<sub>3</sub><sup>-</sup>]<sub>2</sub>-NO<sub>3</sub>)<sup>+</sup>. FT-IR (KBr): 3434, 3026, 2426, 1621, 1587, 1468, 1384, 1304, 1264, 1224, 1080, 1049, 1021, 961, 839, 794, 733, 700, 635, 460 cm<sup>-1</sup>.

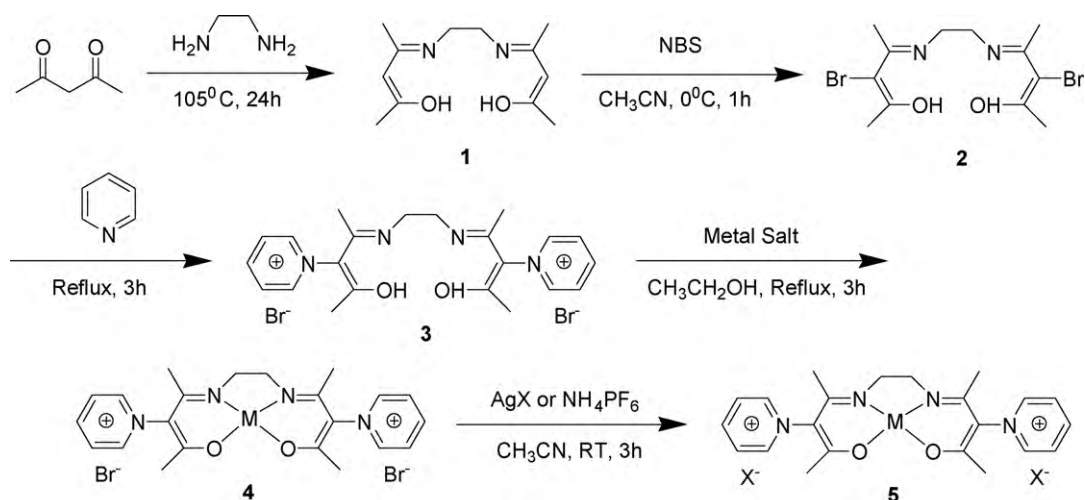
Cu-[Salen-Py][BF<sub>4</sub><sup>-</sup>]<sub>2</sub>: Yield: 87%. Atomic Absorption Spectroscopy: Cu-[Salen-Py][BF<sub>4</sub>]<sub>2</sub>·5H<sub>2</sub>O: Calc. for C<sub>22</sub>H<sub>36</sub>CuF<sub>8</sub>N<sub>4</sub>O<sub>7</sub>: Cu, 9.00%. Found: Cu, 7.53%. ESI-MS, *m/z* = 528.3 (Cu-[Salen-Py][BF<sub>4</sub><sup>-</sup>]<sub>2</sub>-BF<sub>4</sub>)<sup>+</sup>, 220.6 [(Cu-[Salen-Py][BF<sub>4</sub><sup>-</sup>]<sub>2</sub>-2BF<sub>4</sub>)/2]<sup>+</sup>. FT-IR (KBr): 3430, 1623, 1593, 1468, 1384, 1302, 1264, 1124, 1084, 1038, 785, 695, 533, 459 cm<sup>-1</sup>.

Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub>: Yield: 77%. Atomic Absorption Spectroscopy: Cu-[Salen-Py][PF<sub>6</sub>]<sub>2</sub>·5H<sub>2</sub>O: Calc. for C<sub>22</sub>H<sub>36</sub>CuF<sub>12</sub>N<sub>4</sub>O<sub>7</sub>P<sub>2</sub>: Cu, 8.27%. Found: Cu, 8.16%. ESI-MS, *m/z* = 586.4 (Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub>-PF<sub>6</sub>)<sup>+</sup>, 220.7 [(Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub>-2PF<sub>6</sub>)/2]<sup>+</sup>. FT-IR (KBr): 3430, 3060, 1686, 1625, 1595, 1471, 1430, 1355, 1299, 1266, 1223, 1203, 1127, 838, 791, 694, 558, 458 cm<sup>-1</sup>.

Cu-[Salen-Py][CF<sub>3</sub>COO<sup>-</sup>]<sub>2</sub>: Yield: 64%. ESI-MS, *m/z* = 554.3 (Cu-[Salen-Py][CF<sub>3</sub>COO<sup>-</sup>]<sub>2</sub>-CF<sub>3</sub>COO)<sup>+</sup>, 221.0 [(Cu-[Salen-Py][CF<sub>3</sub>COO<sup>-</sup>]<sub>2</sub>-2CF<sub>3</sub>COO)/2]<sup>+</sup>. FT-IR (KBr): 3448, 1685, 1628, 1474, 1432, 1287, 1202, 1139, 842, 798, 726, 459 cm<sup>-1</sup>.

### 2.3. Cyclohexene oxidation catalyzed by Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub>

The Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> were used as catalysts for the allylic oxidation of cyclohexene. In a typical reaction, 40 mmol cyclohexene, 40 ml CH<sub>3</sub>CN, and 0.08 mmol Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> were added into a 100 ml four-neck round bottom reactor, which was fitted with an overhead stirrer and a reflux condenser. The reaction was performed at 78 °C in a water bath with fast stirring. The oxygen was flowing into the reactor at a constant flow rate (20 ml min<sup>-1</sup>). After



**Scheme 2.** Synthesis of M-[Salen-Py][X<sup>-</sup>]<sub>2</sub> (X = Br, NO<sub>3</sub>, BF<sub>4</sub>, CF<sub>3</sub>COO, PF<sub>6</sub>).

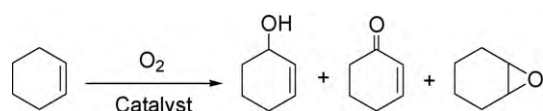
completion of the reaction, the solvent was removed by evaporated under reduced pressure at 60 °C and the products were collected by evaporated under reduced pressure at 100 °C. Subsequently, the catalyst was used without further purification. The progress of reaction was monitored by GC, and the selectivity of 2-cyclohexen-1-ol and 2-cyclohexen-1-one were determined by gas chromatography internal standard method (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

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

Many studies [33–36] found that the catalytic activity of metal-salen complexes depended on the Lewis acidity of the catalyst and the nucleophilicity of the axial ligand. As far as we know, there is little attention on the effect of the counteranion in ionic compound. Due to the unconjugated bond structure between cation and metal center in common metal-salen catalysts modified by ionic compound, the variation of anion almost has no influence on the reactivity of the catalyst. Herein, we proposed a novel metal-salen catalyst modified by ionic compounds (Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub>), whose metal center connected with the cation by conjugate bonds.

The supported catalysts Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> were evaluated in the allylic oxidation of cyclohexene (Scheme 3). As shown in Table 1, we could find that the reactivity of unsupported catalyst Cu-[Salen] was low (Entry 1), in comparison to Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub>. This indicated that ionic salt had been successfully functionalized on the Cu-salen. Based on UV–vis spectra, the charge transfer transition of salen ligand changed from 239 to 268 nm, when ionic salts were functionalized on the salen ligand (see supporting information). It was interesting to find that the type of counteranion could affect the catalytic activity (Entry 2–6). The TOF value for Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub> (45.5) (Entry 2) is more than twice as



**Scheme 3.** The oxidation of cyclohexene.

high as the TOF value for Cu-[Salen-Py][Br<sup>-</sup>]<sub>2</sub> (20.8) (Entry 6). This may be due to the fact that the cation of the ionic salts connected with the metal center by conjugated double bonds, thus the variation via altering the type of counteranion could deliver to the metal center of catalysts. We observed that the catalytic activities of catalysts with different counteranions followed the order in a trend expected of the nucleophilicity of the counteranion in CH<sub>3</sub>CN: PF<sub>6</sub><sup>-</sup> > BF<sub>4</sub><sup>-</sup> > CF<sub>3</sub>COO<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > Br<sup>-</sup> (Entry 2–6) [33–39]. It is worth noting that though the counteranion could improve the catalytic activity of Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub>, in comparison to unsupported catalyst, its selectivity did not lose (selectivity of –ol and –one >90%).

Different counteranions in ionic compounds can change the electric structure of the active center of the catalysts, in turn adjusting the properties of the catalysts via altering the type of counteranion. It is worth noting that altering the counteranion only needs an ion change process with high yield.

An extensive comparison between Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> and the reported ones was carried out then. As shown in Table 2, the homogeneous catalysts showed high activity and selectivity for the oxidation of cyclohexene. However, most of them are difficult to separate from the products. Some of them have been immobilized on the support, however, the heterogeneous catalysts suffered from low activity and selectivity. A new method for immobilizing salen complex onto ionic salt was introduced in this study, and the supported catalysts Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub> displayed satisfied activity and selectivity for the oxidation of cyclohexene (Entry 1). The reaction was carried out continuously and was monitored by GC. After 16 h, the conversion of cyclohexene was up to 100% and the major products were 2-cyclohexen-1-ol and 2-cyclohexen-1-one (Fig. 1).

#### 3.2. Changing the reactivity by solvent-sensitive cation–anion interaction

The ionic compound can be contacted or separated ion pairs in different solvents. It prefers to be contacted ion pairs in low polarity solvent whereas separated in high polarity solvent [45–48]. These findings inspired us to use different solvents to alter the cation–anion interaction, hence improving the catalyst reactivity.

Table 3 summarizes catalytic performances of Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub> and Cu-[Salen-Br] in various solvents. Interestingly, the catalytic activity of Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub> changes in different solvents (Entry 1, 3, 5, 7, 9), whereas the polarity of solvent has no significant influence on the catalytic activity of Cu-[Salen-Br] (Entry 2, 4, 6, 8, 10). The order of the activity of Cu-[Salen-

**Table 1**  
The results of the oxidation of cyclohexene with Cu-[Salen-Py][X<sup>-</sup>] and Cu-[Salen] in CH<sub>3</sub>CN.<sup>a</sup>

Entry	X	Time (h)	Conversion (%)	Selectivity (%)		TOF (h <sup>-1</sup> ) <sup>b</sup>
				-ol	-one	
1	Cu-[Salen]	24	33.6	54.9	41.3	7.0
2	Br <sup>-</sup>	24	100	34.8	58.6	20.8
3	NO <sub>3</sub> <sup>-</sup>	16	100	32.5	60.1	31.3
4	CF <sub>3</sub> COO <sup>-</sup>	14	100	31.9	61.7	35.7
5	BF <sub>4</sub> <sup>-</sup>	13	100	31.3	62.6	38.5
6	PF <sub>6</sub> <sup>-c</sup>	22	100	31.1	63.2	45.5

<sup>a</sup> The oxidation of cyclohexene was performed with cyclohexene (40 mmol), catalyst (2% molar percentage) in 40 ml CH<sub>3</sub>CN at 78 °C.<sup>b</sup> Turnover Frequency (TOF) is calculated by expression of (moles of cyclohexene consumed)/[(mole of catalyst) × time (h)].<sup>c</sup> 1% molar percentage catalyst was used.**Table 2**  
Allylic oxidation of cyclohexene with different kinds of catalysts.<sup>a</sup>

Entry	Catalysts	Reaction conditions	Conversion (%)	Selectivity <sup>b</sup> (%)	TOF (h <sup>-1</sup> ) <sup>c</sup>	Ref.
1	Cu-[Salen-Py][PF <sub>6</sub> <sup>-</sup> ] <sub>2</sub>	22 h (1000:1) <sup>d</sup>	100	94.3	45.5	–
2	Sal-Phe-Mn	12 h (3350:1) <sup>d</sup>	74.8	75.1	208.8	[40]
3	Mn(III) complexes	12 h (5000:1) <sup>d</sup>	82.3	83.7	342.9	[41]
4	{[Ni([16]aneN <sub>5</sub> ) <sub>2</sub> R]}(ClO <sub>4</sub> ) <sub>4</sub>	8 h (8000:1) <sup>d</sup>	53.9	100	359.3	[42]
5	Cobalt resinate	7 h (80:1) <sup>d</sup>	94.5	84.6	10.8	[43]
6	Fe(III)/SiO <sub>2</sub>	10 h (196:1) <sup>d</sup>	98.1	91.9	19.2	[44]

<sup>a</sup> The homogeneous and heterogeneous catalysts used previously and in this study.<sup>b</sup> The selectivity of 2-cyclohexen-1-ol and 2-cyclohexen-2-one.<sup>c</sup> Turnover Frequency (TOF) is calculated by expression of (moles of cyclohexene consumed)/[(mole of catalyst) × time (h)].<sup>d</sup> The ratio of substrate to catalyst.

Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub> in different solvents was CHCl<sub>3</sub> > CH<sub>3</sub>OH > CH<sub>3</sub>CN > DMF (Entry 1, 3, 5, 9), which was contrary to the polarity of solvents. It is mainly because the Cu-[Salen-Py]<sup>+</sup> ··· [PF<sub>6</sub><sup>-</sup>] interaction in Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub> changes in different solvents. High polar solvent could separate [PF<sub>6</sub><sup>-</sup>] from Cu-[Salen-Py]<sup>+</sup>, thus weakening the Cu-[Salen-Py]<sup>+</sup> ··· [PF<sub>6</sub><sup>-</sup>] interaction. As a result, the catalytic activity of Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub> is lower in high polarity solvent. The Cu-[Salen-Br] remains neutral molecule in different solvents, hence the polarity of solvent has little influence on the catalytic activity of Cu-[Salen-Br]. The reactivity of Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub> was not satisfied in CH<sub>3</sub>COOH (Entry 7), due to the fact that CH<sub>3</sub>COOH is apt to be protonated. The proton acted on [PF<sub>6</sub><sup>-</sup>], which could weaken the Cu-[Salen-Py]<sup>+</sup> ··· [PF<sub>6</sub><sup>-</sup>] interaction, thus Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub> had lower activity in CH<sub>3</sub>COOH.

The most interesting results were obtained when Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> were used in different solvents (Table 4). It was found that the reactivity of catalysts with different counteranions were different in CHCl<sub>3</sub> (Entry 1–3) whereas the difference of these catalysts was not so obvious in DMSO (Entry 7–9). The reason is that Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> might be contacted ion pairs in low polarity solvent [45–48] and the direct interaction between anion and cation made the reactivity of the catalyst different from each other. However, in

high polarity solvent, the cation and anion were separated by solvent [45–48], thus the anion had little influence on the reactivity of catalyst.

ESR spectroscopy can give the information about the electronic environment of transition metal, due to the multiplet structure originating from d<sup>n</sup> configuration of the transition metal. The peaks of Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> were quite different from that of Cu-[Salen-Br] both in solid (Fig. 2) and DMSO (Fig. 3). It indicated that ionic compounds significantly affected the electronic environment of Cu. There is a remark shift on the peaks of Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> with different counteranions in solid (Fig. 2) but no significant change in DMSO (Fig. 3). As we know, the anion should directly interact with the cation in solid. The ESR results suggested that the direct interaction can effectively deliver the influence of anion to the metal center. Direct interaction between the anion and cation has been proved to be existent in low polarity solvent [45–48]. Hence, we can expect a direct influence of anion in low polarity solvent, such as CHCl<sub>3</sub>. However, when DMSO was used as solvent, because the anion cannot interact with the cation directly, the influence of different anions was not remark. These ESR results could well explain the above reaction results listed in Table 4, why the difference of the catalytic activity of Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> with various counteranions

**Table 3**  
The results of the oxidation of cyclohexene in different solvents over the complex Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>] and Cu-[Salen-Br].<sup>a</sup>

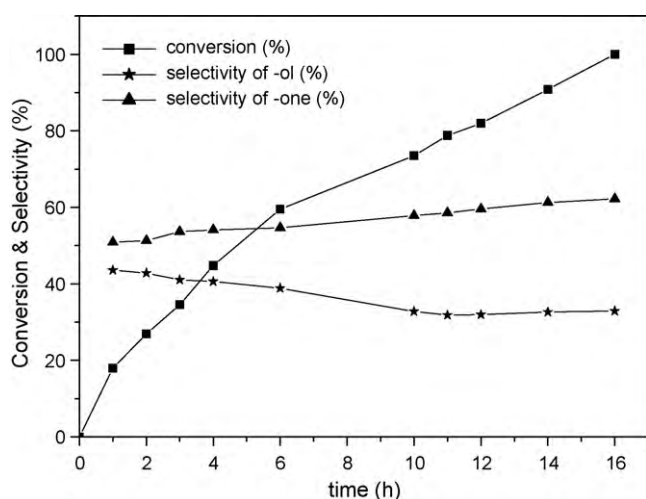
Entry	Catalyst	Solvent	Conversion (%)	Selectivity (%)		TOF (h <sup>-1</sup> ) <sup>b</sup>
				-ol	-one	
1	Cu-[Salen-Py][PF <sub>6</sub> <sup>-</sup> ]	DMF	45.7	38.9	58.2	19.0
2	Cu-[Salen-Br]		29.2	47.6	39.8	12.2
3	Cu-[Salen-Py][PF <sub>6</sub> <sup>-</sup> ]	CH <sub>3</sub> CN	46.1	23.3	62.2	19.2
4	Cu-[Salen-Br]		28.6	25.7	61.1	11.9
5	Cu-[Salen-Py][PF <sub>6</sub> <sup>-</sup> ]	CH <sub>3</sub> OH	48.3	35.1	56.3	20.1
6	Cu-[Salen-Br]		29.0	37.3	53.8	12.1
7	Cu-[Salen-Py][PF <sub>6</sub> <sup>-</sup> ]	CH <sub>3</sub> COOH	25.9	34.8	60.8	10.8
8	Cu-[Salen-Br]		22.1	36.2	54.1	9.2
9	Cu-[Salen-Py][PF <sub>6</sub> <sup>-</sup> ]	CHCl <sub>3</sub>	57.4	31.7	60.8	23.9
10	Cu-[Salen-Br]		29.7	32.3	45.3	12.4

<sup>a</sup> The oxidation of cyclohexene was performed with cyclohexene (40 mmol), catalyst (1% molar percentage) in 40 ml solvent at 58 °C, 24 h.<sup>b</sup> Turnover Frequency (TOF) is calculated by expression of (moles of cyclohexene consumed)/[(moles of catalyst) × time (h)].



**Table 4**The results of the oxidation of cyclohexene over Cu-[Salen-Py][X<sup>-</sup>] with different counteranions in different solvents.<sup>a</sup>

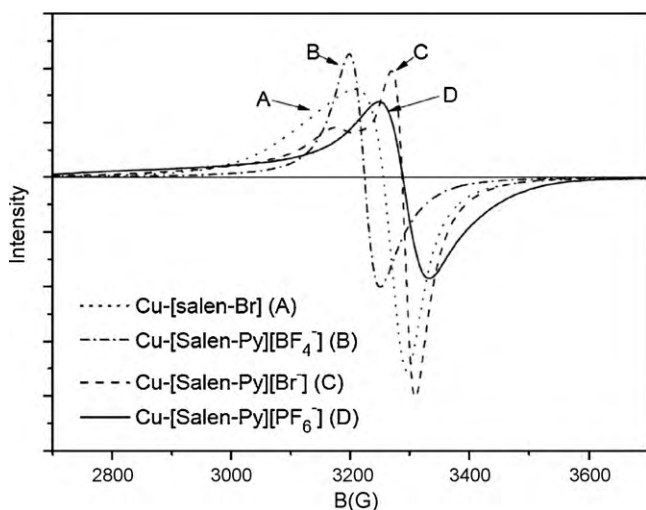
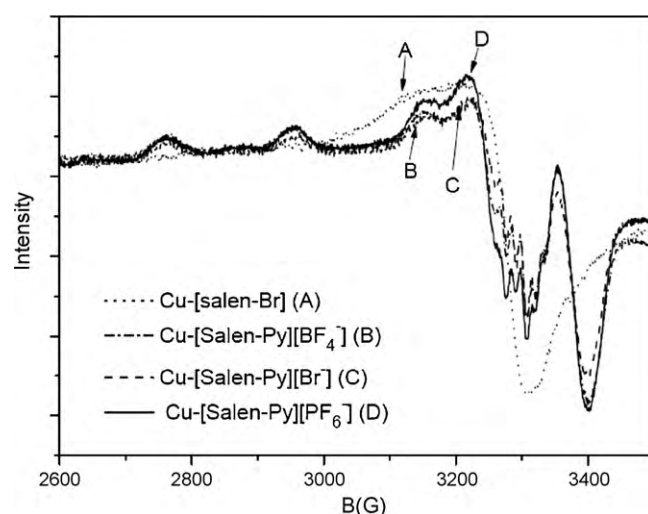
Entry	Anion	Solvent	Conversion (%)	Selectivity (%)		TOF (h <sup>-1</sup> ) <sup>b</sup>
				-ol	-one	
1	Br <sup>-</sup>	CHCl <sub>3</sub>	36.8	33.1	57.7	15.4
2	BF <sub>4</sub> <sup>-</sup>		47.2	31.2	60.2	19.7
3	PF <sub>6</sub> <sup>-</sup>		57.4	31.7	60.8	23.9
4	Br <sup>-</sup>	CH <sub>3</sub> CN	31.7	28.7	59.8	13.2
5	BF <sub>4</sub> <sup>-</sup>		40.3	23.9	61.3	16.8
6	PF <sub>6</sub> <sup>-</sup>		46.1	23.3	62.2	19.2
7	Br <sup>-</sup>	DMSO <sup>c</sup>	56.4	43.7	51.4	11.8
8	BF <sub>4</sub> <sup>-</sup>		58.4	40.0	55.2	12.2
9	PF <sub>6</sub> <sup>-</sup>		70.9	41.9	54.3	14.8

<sup>a</sup> The oxidation of cyclohexene was performed with cyclohexene (40 mmol), catalyst (1% molar percentage) in 40 ml solvent at 58 °C, 24 h.<sup>b</sup> Turnover Frequency (TOF) is calculated by expression of (moles of cyclohexene consumed)/[(mole of catalyst) × time (h)].<sup>c</sup> 2% molar percentage catalyst was used.**Fig. 1.** The conversion and selectivity vs. reaction time plot for oxidation of cyclohexene catalyzed by Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub> in CH<sub>3</sub>CN.

in low polar solvent (CHCl<sub>3</sub>) was higher than in high polar solvent (DMSO).

### 3.3. The effect of axial ligand on Cu-salen

The effects on the activation of the Cu-salen with different axial ligands were evaluated (Table 5). When nitrogen bases were used

**Fig. 2.** ESR spectra of Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> and Cu-[Salen-Br] in solid at 120 K.**Fig. 3.** ESR spectra of Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> and Cu-[Salen-Br] in DMSO at 120 K.

as axial ligands, the reactivity of Cu-salen was not improved. The catalytic activity among the axial ligands followed the order pyridine > 4-methylpyridine > N-methylimidazole (Entry 2, 4, 6), which was contrary to the pK<sub>b</sub> value of the axial ligand. It was interesting to find that the catalytic activity of Cu-salen improved if PF<sub>6</sub><sup>-</sup> was joined as axial ligand, especially for N-methylimidazole (Entry 7). It is worth noting that the catalytic activity of Cu-salen modified by pyridine hexafluorophosphate remarkably improved, in comparison to pyridine hexafluorophosphate as axial ligand (Entry 8). This indicated that ionic salt (pyridine hexafluorophosphate) had been successfully functionalized on the Cu-salen, and the ionic salt could affect the reactivity of the catalyst.

### 3.4. Recycling of the catalyst

One of the features of catalysts modified by ionic compound was that they have almost no vapour pressure and nice thermal stability [17–19]. Thermal analysis had been used to monitor the decomposition profiles of Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> (See supporting information). We could find that the decomposition temperatures of Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> are all higher than 200 °C. Therefore, we could use this thermal stability to recover the catalyst. When the oxidation was completed, the products and solvent were removed by evaporated under reduced pressure, and then the catalyst was reused for subsequent reaction. We took Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub> as catalyst in CH<sub>3</sub>CN for recycling. As shown in Table 6, the Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>]<sub>2</sub> could be reused at least four times with only a slight loss of catalytic activity and selectivity.

**Table 5**  
The results of the oxidation of cyclohexene over Cu-[Salen] with axial ligand.<sup>a</sup>

Entry	Catalyst	Axial ligand	Time (h)	Conversion (%)	Selectivity (%)		TOF (h <sup>-1</sup> ) <sup>b</sup>
					-ol	-one	
1	Cu-[Salen]	None	24	33.6	54.9	41.3	7.0
2	Cu-[Salen]	Pyridine	24	47.7	38.3	52.3	9.9
3	Cu-[Salen]	Pyridine hexafluorophosphate	24	56.9	37.5	54.9	11.9
4	Cu-[Salen]	4-Methylpyridine	24	28.8	44.3	33.1	6.0
5	Cu-[Salen]	4-Methylpyridine hexafluorophosphate	24	32.5	46.2	43.1	6.8
6	Cu-[Salen]	N-Methylimidazole	24	18.3	43.9	35.1	3.8
7	Cu-[Salen]	N-Methylimidazole hexafluorophosphate	24	83.2	19.0	52.3	17.3
8	Cu-[Salen-Py][PF <sub>6</sub> <sup>-</sup> ] <sup>c</sup>	None	22	100	31.1	63.2	45.5

<sup>a</sup> The oxidation of cyclohexene was performed with cyclohexene (40 mmol), catalyst (2% molar percentage), axial ligand (2% molar percentage) in 40 ml CH<sub>3</sub>CN at 78 °C.<sup>b</sup> Turnover Frequency (TOF) is calculated by expression of (moles of cyclohexene consumed)/[(mole of catalyst) × time (h)].<sup>c</sup> 1% molar percentage catalyst was used.**Table 6**  
The recycling studies of Cu-[Salen-Py][PF<sub>6</sub><sup>-</sup>] in the oxidation of cyclohexene.<sup>a</sup>

Entry	Run times	Conversion (%)	Selectivity (%)		TOF (h <sup>-1</sup> ) <sup>b</sup>
			-ol	-one	
1	Fresh	100	31.1	63.2	45.5
2	2nd	100	36.7	54.8	45.5
3	3rd	100	31.6	59.7	45.5
4	4th	95.6	31.8	59.1	43.5
5	5th	88.0	34.8	52.6	40.0

<sup>a</sup> The oxidation of cyclohexene was performed with cyclohexene (40 mmol), catalyst (1% molar percentage) in 40 ml CH<sub>3</sub>CN at 78 °C for 22 h.<sup>b</sup> Turnover Frequency (TOF) is calculated by expression of (moles of cyclohexene consumed)/[(mole of catalyst) × time (h)].

## 4. Conclusions

The salen complexes modified by ionic compound M-[Salen-Py][X<sup>-</sup>] were synthesized, and this kind of catalysts provided high activity and selectivity for the allylic oxidation of cyclohexene. The types of counteranion in ionic compounds could affect the catalytic activity of the catalysts, especially, the highest nucleophilicity PF<sub>6</sub><sup>-</sup> gave the best catalytic activity. The polarity of solvent could also change the cation-anion interaction, and this can be used to improve the reactivity of catalysts. The differences of the catalytic activity of Cu-[Salen-Py][X<sup>-</sup>]<sub>2</sub> with various counteranions in low polarity solvent were remarkable, however, the counteranion had little influence in high polarity solvent. Thus, if it is desired to exclude the influence of anion, the solvent with high dielectric constant is recommended. If it is anticipated that the reaction is influenced mainly by the cooperation between the cation and anion, the solvent with low dielectric constant is preferential. Moreover, the catalyst could be used at least four times without significant loss of catalytic activity and selectivity. These observations suggested that the easily reconstructed complexes presented here are promising catalysts for allylic oxidation of cyclohexene.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.05.006.

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