吡唑-3-甲酸 Cu(II)/Mn(II)配合物的合成、表征及常压下对二氧化碳催化转化

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摘要: 合成和表征了 2 个吡唑-3-甲酸过渡金属配合物[Cu$_2$(pca)$_2$(H$_2$O)$_6$]·2H$_2$O (**1**),[Mn(Hpca)$_2$(phen)]·3H$_2$O (**2**)(H$_2$pca=吡唑-3-甲酸;phen=菲咯啉)。X 射线单晶衍射分析结果表明,配合物 **1** 属于单斜晶系 $P2_1/n$ 空间群,它是一个畸变八面体的双核铜配合物;配合物 **2** 是一个畸变八面体的单核锰配合物。配合物 **1** 和 **2** 分别通过分子间的 O−H⋯O,N−H⋯O 氢键形成了三维网状结构。配合物 **1** 在二氧化碳的环加成反应中显示出了良好的催化效率(转化率高达 97.4%;选择性高达 98.9%)。

关键词: 吡唑-3-甲酸;配合物;晶体结构;二氧化碳转化

Cu(II)/Mn(II) Complexes Formed by Pyrazole-3-carboxylic Acid: Syntheses, Characterization and Highly Efficient Conversion of CO$_2$ at Atmospheric Pressure

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Abstract: Two transition metal complexes: Cu$_2$(pca)$_2$(H$_2$O)$_6$·2H$_2$O (**1**) and Mn(Hpca)$_2$(phen)·3H$_2$O (**2**) (H$_2$pca= pyrazole-3-carboxylic acid; phen=phenanthroline) have been prepared based on pyrazole-3-carboxylic acid and structurally characterized. The single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the monoclinic system $P2_1/n$ space group and the binuclear copper center in **1** and mononuclear Mn(II) center in **2** possess the distorted octahedral geometry. The three dimensional 3D framework of **1** and **2** are formed by the intermolecular O−H⋯O, N−H⋯O hydrogen bonding interactions. Importantly, complex **1** exhibits excellent heterogeneous catalytic performance　(Conversion: up to 97.4%, Selectivity: up to 98.9%) in the catalytic conversion of CO$_2$ to cyclic carbonate. CCDC: 1055764, **1**; 1055766, **2**.

Keywords: pyrazole-3-carboxylic acid; complex; crystal structure; conversion of CO$_2$

0 Introduction

In the last few decades, transition metal complexes have been highlighted by many researchers, owing to their outstanding abilities in gas storage, molecular recognition, structure analysis and catalysis[1-3]. The combination of transition metal ions and organic ligands in many systems has not only led to more complicated and fascinating structural topologies, but also exerted synergetic effects and merged the merits of both aspects, which reveal potential applications in heterogeneous catalysis, selective absorption, and photonic, electronic, and magnetic functional materials[4-6]. Among lots of organic ligands, pyrazole carboxylates play a key role in generating the excellent architectures because they not only possess potential coordination nodes and the strong coordination ability, but also can be acted as the multiple proton donors, acceptors and build high-dimensional supramolecular frameworks. However, to our best knowledge, transition metal coordination complexes derived from pyrazole-3-carboxylic acid are very little[7-8], and the studies of catalytic properties of the transition metal coordination complexes are rather rare.

Herein, copper(II) and manganese(II) complexes **1** and **2** formed by pyrazole-3-carboxylic acid, namely, $[Cu_2(pca)_2(H_2O)_6] \cdot 2H_2O$ (**1**) and $[Mn(Hpca)_2(phen)] \cdot 3H_2O$ (**2**), have been synthesized and structurally characterized. Additionally, two complexes were further investigated as heterogeneous catalysts for the synthesis of cyclic carbonates from epoxides at CO_2 atmospheric pressure.

1 Experimental

1.1 General methods and materials

All reagents and solvents for synthesis were purchased from commercial sources and used without further purification. The FT-IR spectra were recorded from KBr pellets in the range of 4 000~400 cm^{-1} on Nicolet 170 SXFT/IR spectrometer. The GC analyses were performed on Shimadzu GC-2014C with a FID detector equipped with an Rtx-1701 Sil capillary column. The C, H and N elemental analyses were conducted on Perkin-Elmer 240C elemental analyzer.

1.2 Synthesis

Complex $[Cu_2(pca)_2(H_2O)_6] \cdot 2H_2O$ (**1**): To a solution of NaOH (0.004 g, 0.1 mmol) and H_2pca (0.044 8 g, 0.4 mmol) in water (4 mL), $Cu(NO_3)_2 \cdot 3H_2O$ (0.096 6 g, 0.4 mmol) and H_2O (5 mL) were sequentially added in a 25 mL glass beaker. The reaction mixture was stirred for 1 h at room temperature and filtrated. After that, the blue block crystals of **1** were obtained by slow evaporation of the filtrate over three weeks. The yield was *ca.* 23% based on Cu. IR (KBr, cm^{-1}): 3 484 (s), 1 659 (s), 1 555 (w), 1 507 (m), 1 475 (m), 1 382 (s), 1 355 (s), 1 263 (s), 1 232 (w), 1 133 (m), 1 068 (m), 1 014 (m), 942 (m), 898 (m), 839 (m), 785 (m), 649 (w), 501 (w). Anal. Calcd. for $C_8H_{20}Cu_2N_4O_{12}$(%): C 19.55, H 4.10, N 11.40; Found (%): C 19.61, H 4.16, N 11.33.

Complex $[Mn(Hpca)_2(phen)] \cdot 3H_2O$ (**2**): H_2pca (0.022 4 g, 0.2 mmol), $Mn(OAc)_2 \cdot 4H_2O$ (0.024 5 g, 0.1 mmol), 1,10-Phenanthroline (0.019 8 g, 0.1 mmol) and distilled water (10 mL) were sealed in a 23 mL Teflon-lined steel vessel and heated at 180 ℃ for 72 h, and then cooled to room temperature at a rate of 0.1 ℃·min^{-1}. The resulting colorless block crystals of **2** were obtained, washed with distilled water and then air-dried. The yield was *ca.* 35% based on Mn. IR (KBr, cm^{-1}): 3 145 (s), 1 610 (s), 1 517 (m), 1 494 (m), 1 464 (w), 1 424 (m), 1 361 (s), 1 249 (m), 1 142 (w), 1 103 (m), 998 (m), 927 (w), 865 (w), 846 (m), 726 (m), 638 (w), 468 (w). Anal. Calcd. for $C_{20}H_{20}MnN_6O_7$(%): C 46.97, H 3.94, N 16.43; Found (%): C 47.06, H 3.99, N 16.35.

1.3 Catalytic conversion of CO_2 to cyclic carbonate

The reactions were carried out in a 10 mL three-necked glass flask with reflux and CO_2 bubbling. Epoxides (10 mmol), catalyst (10%, *n/n*, the same below), Bu_4NBr(4%), and biphenyl (1 mmol, internal standard for quantitative analysis by gas chromatography) were successively added. The reaction mixture was kept stirring at 333 K for 24 h. Upon completion, the reactant and catalyst were separated by centrifugation, washed with CH_2Cl_2, and air-dried. The

supernatant was diluted by 25 mL acetonitrile and quantitatively analyzed by GC and GC-MS.

1.4　X-ray crystallography

Single-crystal X-ray diffraction data for complexes **1**~**2** were conducted on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo $K\alpha$ radiation　(λ=0.071 073 nm) at 296 K. All absorption corrections were applied using multi-scan technique. The structures were solved by the direct method and refined through full-matrix least-squares techniques method on F^2 using the SHELXTL 97 crystallographic software package[9-10]. The hydrogen atoms of the organic ligands were refined as rigid groups. Crystallographic data for complexes **1** and **2** are summarized in Table 1, and the selected bond distances and bond angles of complexes **1** and **2** are listed in Table 2.

CCDC: 1055764, **1**; 1055766, **2**.

Table 1　Crystallographic data for complexes 1 and 2

	1	2
Formula	$C_8H_{20}Cu_2N_4O_{12}$	$C_{20}H_{20}MnN_6O_7$
Formula weight	491.36	511.36
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a / nm	0.822 02(6)	1.031 70(9)
b / nm	0.911 52(7)	1.310 61(12)
c / nm	1.212 18(11)	1.769 19(15)
β / (°)	107.143(2)	108.231(3)
V / nm^3	0.867 92(12)	2.272 1(3)
Z	2	4
D_c / (g·cm^{-3})	1.880	1.495
μ / mm^{-1}	2.519	0.635
$F(000)$	500	1 052
Reflections collected, unique	4 717, 1 522 (R_{int}=0.125 6)	11 134, 4 006 (R_{int}=0.040 6)
Largest diff. peak and hole / (e·nm^{-3})	1 443 and −1 215	359 and −260
Goodness of fit on F^2	1.048	1.052
Final R indices [$I>2\sigma(I)$]	R_1=0.084 2, wR_2=0.195 2	R_1=0.042 8, wR_2=0.085 3
R indices (all data)	R_1=0.142 2, wR_2=0.255 9	R_1=0.082 4, wR_2=0.105 8

Table 2　Selected bond distances (nm) and bond angles (°) for complexes 1 and 2

Complex **1**					
Cu(1)-N(2)^i	0.202 9(8)	Cu(1)-N(1)	0.204 2(8)	Cu(1)-O(4)	0.206 6(6)
Cu(1)-O(3)	0.207 9(7)	Cu(1)-O(1)	0.210 2(7)	Cu(1)-O(5)	0.214 5(7)
N(2)^i-Cu(1)-N(1)	97.5(3)	N(2)#1-Cu(1)-O(4)	92.9(3)	N(1)-Cu(1)-O(4)	96.9(3)
N(2)#1-Cu(1)-O(3)	93.3(3)	N(1)-Cu(1)-O(3)	168.9(3)	O(4)-Cu(1)-O(3)	84.8(3)
N(2)^i-Cu(1)-O(1)	176.6(3)	N(1)-Cu(1)-O(1)	79.3(3)	O(4)-Cu(1)-O(1)	88.6(3)
O(3)-Cu(1)-O(1)	89.9(3)	N(2)^i-Cu(1)-O(5)	93.2(3)	N(1)-Cu(1)-O(5)	92.1(3)
O(4)-Cu(1)-O(5)	168.5(3)	O(3)-Cu(1)-O(5)	85.0(3)	O(1)-Cu(1)-O(5)	85.9(3)
Complex **2**					
Mn(1)-O(3)	0.215 4(2)	Mn(1)-N(6)	0.224 1(3)	Mn(1)-O(1)	0.217 3(2)
Mn(1)-N(3)	0.227 7(3)	Mn(1)-N(1)	0.223 2(3)	Mn(1)-N(5)	0.229 5(3)
O(3)-Mn(1)-O(1)	103.65(9)	N(1)-Mn(1)-N(3)	158.24(9)	O(3)-Mn(1)-N(1)	93.27(9)
N(6)-Mn(1)-N(3)	100.81(9)	O(1)-Mn(1)-N(1)	74.26(9)	O(3)-Mn(1)-N(5)	88.82(10)

Continued Table 2

| O(3)-Mn(1)-N(6)	161.41(9)	O(1)-Mn(1)-N(5)	167.53(10)	O(1)-Mn(1)-N(6)	94.34(10)
N(1)-Mn(1)-N(5)	105.88(10)	O(3)-Mn(1)-N(3)	74.62(9)	N(3)-Mn(1)-N(5)	92.12(9)
O(1)-Mn(1)-N(3)	90.82(9)				

Symmetry codes: ^{i} −x+1, −y+1, −z+1 for **1**

2 Results and discussion

2.1 Structure description

The single-crystal X-ray diffraction reveals the asymmetric unit of complex **1** consists of one crystall-ographic independent Cu^{2+} cation, one pca^{2-} anion, three coordination water molecules and one free water molecule (Fig.1a). The Cu^{2+} cation, which coordinated by oxygen atom (O1), nitrogen atom (N1) from pca^{2-}
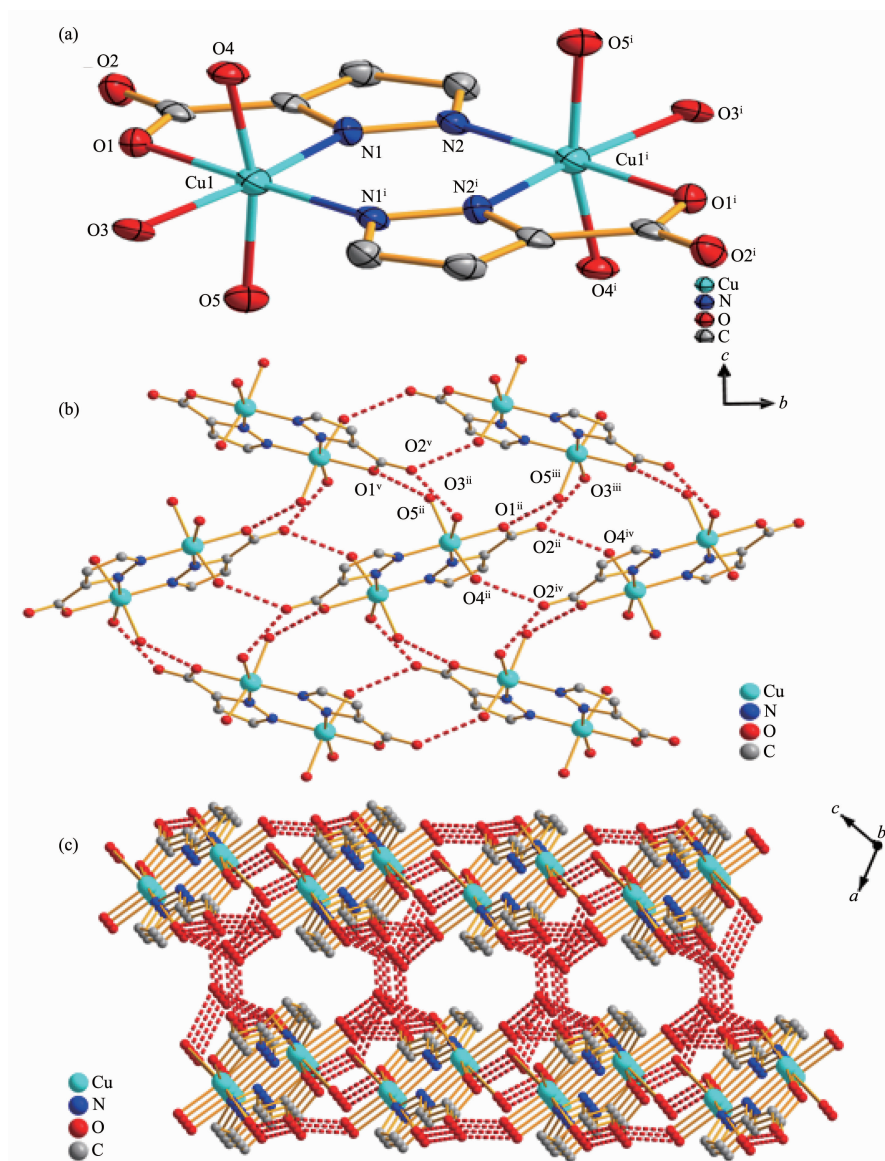
Hydrogen atoms and free water molecules are omitted for clarity; Symmetry codes: ^{i} 1−x, 1−y, 1−z; ^{ii} 1.5−x, −0.5+y, 0.5−z; ^{iii} 1+x, y, z; ^{iv} 0.5+x, 1.5−y, −0.5+z; ^{v} 1+x, −1+y, z

Fig.1 (a) Coordination environment of the Cu^{2+} ions in **1** with thermal ellipsoids at 50% probability level; (b) Two dimensional supramolecular layer of **1** formed by hydrogen bonds in the bc plane; (c) Three dimensional supramolecular framework of **1** consisting of tetrahedral water clusters

anion, nitrogen atom (N2a) from the other pca^{2-} anion and three oxygen atoms (O3, O4, O5) from three coordination water molecules, displaying a distorted {CuO$_4$N$_2$} octahedral coordination geometry. The distances of the Cu-O and Cu-N are 0.206 6(6)~0.214 5(7) nm and 0.202 9(8)~0.204 2(8) nm, respectively, which are similar with those of reported complexes[11-12]. The bond angles around Cu^{2+} cation are in the range of 79.3(3)°~176.6(3)°. The six-membered ring of complex **1**, which is formed by four pyrazole nitrogen atoms of two pca^{2-} ligand and two Cu^{2+} cations, is similar with that of the complex [Cu(NAA)$_2$(bim)$_2$]·H$_2$O (HNAA = anaphthylacetic acid, bim=benzimidazole)[13]. However, the distance of Cu···Cu (0.400 76 nm) in **1** is longer than that of the reported copper complex[14]. The oxygen atoms (O3, O4, O5) link the carboxylic oxygen atoms (O1, O2) to form the 2D supramolecular layer through O−H···O hydrogen bonding interactions (O3···O2 0.267 0(3) nm, O4···O2 0.276 9(4) nm, O5···O1 0.276 5(1) nm) (Fig.1b, Table 3). The free water molecules further connect the neighboring 2D supramolecular layers to generate 3D supramolecular framework via the hydrogen bonding interactions (Fig.1c) (O4··· O6 0.275 3(6) nm, O5···O6 0.278 8(3) nm, O6···O2

0.285 9(7) nm, O6···O3 0.288 7(1) nm) (Table 3).

Single-crystal X-ray diffraction exhibits that complex **2** crystallizes in the monoclinic crystal system with $P2_1/c$ space group. The crystal structure of **2** is composed of one Mn^{2+} cation, one phen ligand, two Hpca$^-$ anions and three lattice water molecules (Fig.2a). The Mn^{2+} center shows a distorted {MnO$_2$N$_4$} octahedral coordination geometry and coordinated with two nitrogen atoms (N1, N3) from two separate Hpca$^-$ anions, two chelate nitrogen atoms (N5, N6) from phen ligand and two carboxylic oxygen atoms (O1, O3). The bond distances of the Mn-O and Mn-N are 0.215 4(2) ~0.217 3(2) nm and 0.223 2(3)~0.229 5(3) nm, respectively. The bond angles around Mn^{2+} cation are in the range of 73.20(10)°~167.53(10)°. The Mn^{2+} cation is coordinated with Hpca$^-$ anion and phen ligand to form three five-membered rings. Interestingly, the hexanuclear chair-like water clusters are formed by the intermolecular hydrogen bonding interaction of free water molecules in the complex **2** (O6···O7 0.275 2(4) nm, O7···O5 0.288 0(2) nm, O7···O5 0.272 4(5) nm). Furthermore, a 3D supramolecular framework is formed by the oxygen atoms (O5, O6) of the hexanuclear water clusters and the carboxylic oxygen atoms (O1,

Table 3　Hydrogen-bonding geometry for complexes 1 and 2

D−H···A	d(D-H) / nm	d(H···A) / nm	d(D···A) / nm	∠D−H···A / (°)
Complex **1**				
O(3)−H(3C)···O(2)^i	0.085 0	0.182 7	0.267 0(3)	170.99
O(4)−H(4C)···O(2)^{ii}	0.085 0	0.192 7	0.276 9(4)	170.86
O(5)−H(5C)···O(1)^i	0.085 0	0.191 9	0.276 5(1)	173.31
O(4)−H(4D)···O(6)	0.085 0	0.190 9	0.275 3(6)	171.48
O(5)−H(5D)···O(6)^{iii}	0.085 0	0.194 2	0.278 8(3)	173.77
O(6)−H(6C)···O(2)^{iv}	0.085 0	0.201 8	0.285 9(7)	170.16
O(6)−H(6D)···O(3)^v	0.085 0	0.207 3	0.288 7(1)	160.26
Complex **2**				
O(6)−H(6D)···O(7)^i	0.085 0	0.190 7	0.275 2(4)	172.79
O(7)−H(7C)···O(5)^{ii}	0.085 0	0.203 2	0.288 0(2)	175.73
O(7)−H(7D)···O(5)^{iii}	0.085 0	0.189 7	0.272 4(5)	163.87
O(5)−H(5D)···O(4)^{ii}	0.085 0	0.191 6	0.275 9(0)	171.46
O(5)−H(5C)···O(1)	0.085 0	0.189 6	0.273 8(9)	171.38
O(6)−H(6C)···O(2)^{iv}	0.085 0	0.185 1	0.269 7(2)	173.34
N(2)−H(2)···O(6)	0.086 0	0.181 2	0.265 4(9)	165.97

Symmetry codes: ^{i} −x+1/2, y−1/2, −z+1/2; ^{ii} −x+1, −y+2, −z+1; ^{iii} −x+1, −y+1, −z+1; ^{iv} x−1/2, −y+3/2, z+1/2; ^{v} x+1/2, −y+3/2, z+1/2 for **1**; ^{i} x, y+1, z; ^{ii} −x+1, y−1/2, −z+3/2; ^{iii} x, −y+1/2, z−1/2; ^{iv} x, −y+3/2, z−1/2 for **2**.
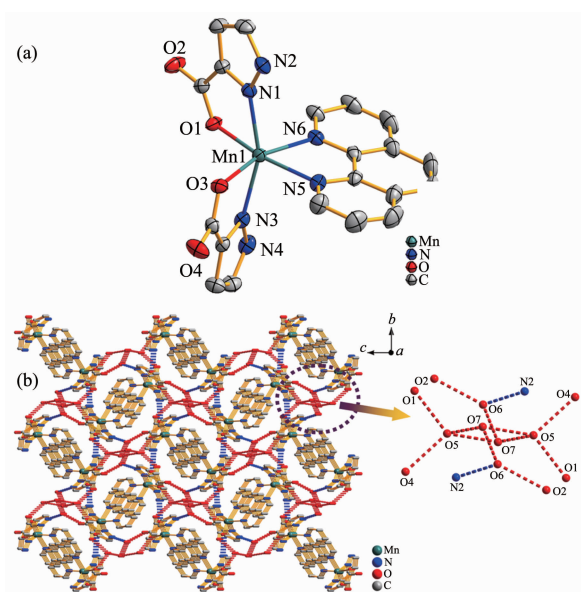
Hydrogen atoms and lattice water molecules are omitted for clarity

Fig.2 (a) Coordination environment of the Mn^{2+} ions in **2** with thermal ellipsoids at 50% probability level; (b) Three dimensional supramolecular framework of **2** consisting of $(H_2O)_6$ clusters

O2, O4) and the pyrazole nitrogen atoms (N2) of the adjacent molecule (O5⋯O4 0.275 9(0) nm, O5⋯O1 0.273 8(9) nm, O6⋯O2 0.269 7(2) nm, N2⋯O6 0.265 4(9) nm) (Fig.2b, Table 3).

2.2 Catalytic conversion CO_2 to cyclic carbonate catalyzed by complexes 1 and 2

Carbon dioxide is not only the main greenhouse gas, but also is an attractive C1 building block in organic synthesis as it is highly functional, abundant, inexpensive, nontoxic, and nonflammable. Chemical fixation of CO_2 to obtain the valuable chemical materials is of both scientific and practical significance[15]. One of the most promising pathways is the synthesis of cyclic carbonate from CO_2 and epoxide. Thus-obtained five-membered cyclic carbonates can serve as valuable monomers for polycarbonates and electrolytes in secondary batteries and chemical sources[16-17]. Our cycloaddition studies focused on the case of cycloaddition of CO_2, with the aim to understand the catalytic property of pyrazole-3-carboxylic acid complexes for developing a new cycloaddition system in organic chemistry. The reactions were performed in a 10 mL flask in the presence of Bu_4NBr. To optimize

the product conversion and selectivity, the cycloaddition of CO_2 to styrene oxide to styrene carbonate was selected as a model reaction to evaluate the catalytic activities of the different catalysts in the presence of Bu_4NBr (Scheme 1). The influences of different reaction conditions about the cycloaddition of CO_2 to styrene carbonate have been investigated. The conversion and selectivity of each reaction are summarized and illustrated in Fig.3. After the preliminary optimization, the best conversion of styrene oxide (95.1%) was obtained during the cycloaddition of CO_2 to styrene carbonate (10 mmol), with catalyst **1** (10%) and 4% Bu_4NBr at 333 K for 24 h.
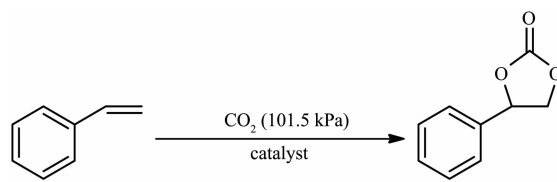
Scheme 1 Conversion of styrene oxide to styrene carbonate
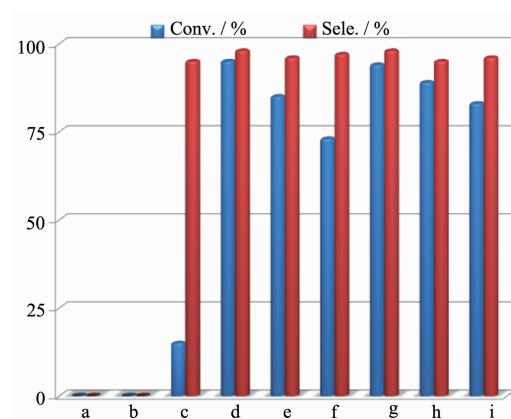
Reaction conditions: styrene oxide (10 mmol), 333 K, 24 h; (a) Blank, (b) $Cu(OAc)_2$(10%), (c) Bu_4NBr (4%), (d) catalyst **1** (10%) and Bu_4NBr (4%), (e) catalyst **2** (10%) and Bu_4NBr (4%), (f) catalyst **1** (8%) and Bu_4NBr (4%), (g) catalyst **1** (12%) and Bu_4NBr (4%), (h) catalyst **1** (10%) and Bu_4NI (4%), (i) catalyst **1** (10%) and Bu_4NCl (4%)

Fig.3 Conversion and selectivity of styrene oxide to styrene carbonate with different reaction conditions

Furthermore, control catalytic experiments of the cycloaddition of styrene oxide were performed under the same reaction conditions. No styrene carbonate was detected in the absence of Bu_4NBr (Fig.3a, 3b); The conversion was 16.7% in the absence of the

catalyst, when the Bu₄NBr was used as catalyst (Fig. 3c), which is consistent with the previous reports[18]. However, using the complex **1**, the reaction can be finished in 24 h and the conversion reaches 95.1%, which overmatch the Cu(OAc)₂ and complex **2**. Based on the above-mentioned facts, we conclude that the introduce of pyrazole-3-carboxylic acid ligand into the framework bring new coordination environment for the copper ions, which can enhance its catalytic capacity for the reaction material when combined with Bu₄NBr. And indeed, catalytic activities of the complex **1** outperforms many effective catalysts, *i.e.* ionic liquid/ Zn-PPh₃ catalysts[19], [Dmim]₂ZnBr₂Cl₂[20] and pyridinium -based ionic liquids catalyst[21].

　　As a green catalyst, complex **1** was further used to explore the influence of catalyst recycles on the catalytic properties of cycloaddition of styrene oxide in a heterogeneous system. In the recycle experiments, the catalyst can easily be separated by filtration or centrifugation and washed using CH₂Cl₂. The IR spectra of the recovered complex **1** were identical to those of the freshly prepared complex **1** (Fig.4). The experiment results displayed that no obvious loss of activity was observed after three runs (Conv. 95.1% for 1st, 94.8% for 2nd, 94.5% for 3rd) as shown in Fig.5.
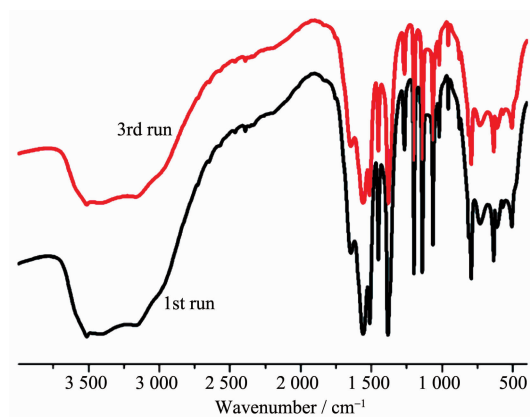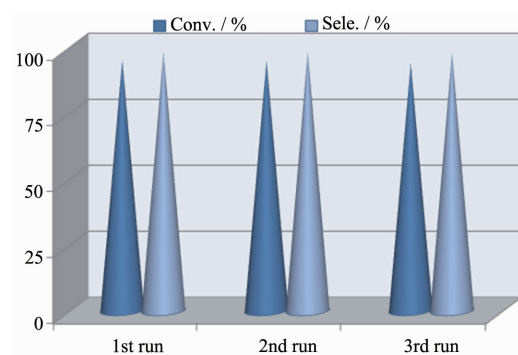

Fig.4　FT-IR spectra of complex **1** after three runs of catalytic cycles

Reaction conditions: styrene oxide (10 mmol), catalyst **1** (10%) and Bu₄NBr (4%), 333 K, 24 h

Fig.5　Recycle experiments of complex **1** on conversion of styrene oxide to styrene carbonate

　　Following the success of styrene epoxide

Table 4　Results of cycloaddition of epoxides catalyzed by complex 1ᵃ

Entry	Epoxide	Product	Conv. / %	Sele. / %b
1			92.9	98.7
2			95.1	98.2
3			97.4	98.9
4			19.6	97.5

ᵃ Reaction conditions: epoxides (10 mmol), complex **1** (10%), 333 K, Bu₄NBr (4%), 24 h; ᵇ Selectivity to cyclic carbonate.

cycloaddition and evaluating the scope and limitations of the current procedure, cycloaddition reactions with an array of epoxy compounds were examined using complex **1**. A series of epoxide substrates were examined for the synthesis of corresponding cyclic carbonates (Table 4). Cyclic carbonates with alkyl side chain groups, aryl side chain groups were successfully synthesized from corresponding epoxides in high conversion (up to 97.4%) and selectivity (up to 98.9%). The di-substituted epoxide, gave lower activity toward the production of the corresponding cyclic carbonates, which is presumably due to the effect of the high steric hindrance. These preliminary results exhibit that complex **1** and Bu_4NBr can facilitate the cycloaddition of epoxides and serve as highly efficient and selective catalysts at CO_2 atmospheric pressure (101.5 kPa).

3　Conclusions

In summary, $Cu(II)/Mn(II)$ complexes formed by pyrazole-3-carboxylic acid have been successfully synthesized and found that the pyrazole-3-carboxylic acid copper complexes can used as catalysts for highly efficient (Conv. 90.5%~94.8%) and excellent selective (Sele. 93.5%~98.3%) conversion of CO_2. The other pyrazole-3-carboxylic acid transition metal complexes are in process, which will be reported timely.

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