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ARTICLE

2D Co-based coordination polymer with histidine derivative as an efficient heterogeneous catalyst for the oxidation of cyclohexene

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Fan Yu,[a,*] Xin Xiong,[a] Kexing Huang,[a] Yinliu Zhou,[a] and Bao Li[b,*]

Abstract: Hydrothermal reaction of $CoCl_2$ and 4-((1-carboxy-2-(1H-imidazol-4-yl)ethylamino)methyl)benzoic acid (H_2L) generated a $\{Co_2(H_2O)\}$-based 2D coordination framework, $\{(Co(L)(H_2O))_2(H_2O)\}_n$ (**1**). Heterogenous catalytic experiments on allylic oxidation of cyclohexene show that activated **1** exhibits highly catalytic activity using *tert*-butylhydroperoxide (*t*-BuOOH) as oxidant toward formation of *tert*-butyl-2-cyclohexenyl-1-peroxide. The activation energy for the oxidation of cylcohexene with **1** catalyst was approximately calculated as 91.98 kJ mol^{-1}. This work demonstrates that creativity of coordinatively unsaturated metal sites in CPs could significantly enhance heterogeneous catalytic activity and selectivity.

Introduction

Catalytic oxidation of cyclohexene into value-added oxygenated derivatives is particularly important and extensively investigated because its oxidation products are useful intermediates in organic synthesis and the fragrance industry.[1] The traditional catalytic procedures produce a large number of environmental pollutants during the process of oxidation. Therefore, the development of effectively green processes for the catalytic oxidation of alkenes is becoming urgently necessary.[2] Many studies have revealed that transition metal complexes containing redox active transition metals are important homogenous catalysts which could selectively oxidize cyclohexene to the specific oxydates.[3,4] However, the performance of these catalysts is still limited, and the recovery of the catalysts from the reaction systems is very difficult since the oxidation reactions are usually performed in the liquid phase. Based on the environmental and economic considerations, heterogeneous catalysts are desired to improve the effect.[5,6] Currently, it is still very hard for the synthesis of effectively green heterogeneous catalysts since the troublesome synthesis process and unclear catalytic mechanism of heterogeneous catalysts. Therefore, to probe the effective catalysts and explain the detailed catalytic mechanism becomes the main challenge in a heterogeneous catalytic system.[7]

In the past decades, coordination polymers (CPs) have been attracting great attention owing to their potential applications in various scientific research fields. Recently, CPs based heterogeneous catalysts have been also investigated due to its catalytically active sites and accessible processing methods.[8] Though an amount of interesting and novel catalysts based on CPs have been explored, the rational design of CPs based heterogeneous catalysts with high catalytic performance under mild reaction conditions, environmental benignity and easy operation procedures still remains a painful challenge.[9]

In the transitional metal complexes utilized as heterogeneous catalysts, cobalt based CPs attract great attention.[10,11] Co(II) atoms could adopt varied coordination geometries such as octahedral, tetrahedral, square-pyramidal, trigonal-bipyramidal and square-planar, which makes it easy to bear unsaturated coordination sites with catalytic activity.[12,13] With all the above considerations in mind, we selected histidine derivatives, 4-((1-carboxy-2-(1H-imidazol-4-yl)ethylamino)methyl)benzoic acid (H_2L), acted as the organic linker to produce the cobalt based CPs. The amino acid derivative was produced via adorning auxiliary coordinative group as benzoate on the amino acid scaffold. Through the published research results related with the amino acid derivatives, this kind of ligands reserves the classical N-O chelate coordinate mode and possesses large bulk effect, which could be easy to result in CPs with remnant coordinative sites and much more stabilization.[14] In consistent with our assumption, a 2D cobalt(II) based CP, $\{(Co(L)(H_2O))_2(H_2O)\}_n$ (**1**), had been successfully constructed by the utilization of the designed derivative. Single-crystal X-ray diffraction studies reveal that water molecules were finally coordinated on the cobalt ion, which could be easily activated via heat. Subsequently, particular attention is given to investigate the effect of activated cobalt based heterogeneous catalyst in the

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[a] *Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, School of Chemical and Environmental Engineering Jianghan University, Wuhan, 430056, PR China*
Email:yufan0714@163.com
[b] *Address here.Department of Chemistry and Chemical Engineering Huazhong University of Science and Technology , wuhan, hubei, 430074, PR China.*
E-mail: libao@hust.edu.cn.

† Footnotes relating to the title and/or authors should appear here.

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allylic oxidation of cyclohexene using *tert*-butylhydroperoxide (*t*-BuOOH) as oxidant and selectively catalyzes the oxidation reaction toward formation of *tert*-butyl-2-cyclohexenyl-1-peroxide. Furthermore, we presented a probable mechanism to illustrate the high catalytic activation and selectivity for the **1** catalytic oxidation. In order to compare the catalytic activity of **1**, an isomorphic Mn-based CP, $\{(Mn(L)(H_2O))_2(H_2O)\}_n$ (**2**), had been also constructed and utilized as the catalyst in the oxidation of cyclohexene under the same experiment condition. Catalytic results reveal much lower effect compared with **1**.

Table 1. Crystal data of 1 and 2

	1	2
Chemical formula	$C_{28}H_{32}Co_2N_6O_{11}$	$C_{28}H_{32}Mn_2N_6O_{11}$
Formula Mass	746.46	742.41
Crystal system	Monoclinic	Monoclinic
a/Å	22.089(13)	22.4588(11)
b/Å	6.142(4)	6.1786(4)
c/Å	13.906(9)	14.1282(7)
β/°	125.968(9)	127.551(4)
Unit cell volume/$Å^3$	1527.0(16)	1554.29(15)
Space group	$C2$	$C2$
Z	2	2
No. of reflections measured	5487	1275
No. of independent reflections	2954	1275
Final R_1 values ($I > 2\sigma(I)$)	0.0606	0.0624
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1639	0.1769
Final R_1 values (all data)	0.0715	0.0640
Final $wR(F^2)$ values (all data)	0.1796	0.1806

Results and discussion

Synthesis of 1

The complex **1** and **2** was synthesized by hydrothermal reaction at 90 ℃. The compositions of **1** and **2** were further deduced from single crystal X-ray diffraction, elemental analyses, and IR spectrum. Crystal data are listed in Table 1. The broad bands in the 3579-3534, 3449-3331 and 3103-2883 cm^{-1} region are assigned to the O-H, N-H and C-H stretching vibrations, respectively. The IR spectra also show characteristic absorption bands mainly attributed to the asymmetric (vas: ca. 1600 cm^{-1}) and symmetric (vs: ca. 1385 cm^{-1}) stretching vibrations of the carboxylate groups. No band in the region 1690–1730 cm^{-1}, indicates complete deprotonation of the carboxylate groups, and is consistent with the result of the X-ray diffraction analysis.

Crystal structure of 1 and 2

Single crystal X-ray diffraction results indicate that complexes **1** and **2** are isostructural with similar cell parameters and asymmetric units. Herein, the detailed structural description of complex **1** as the example had been presented. Compound **1** crystallizes in the monoclinic space group *C*2. The asymmetric unit of **1** contains one histidine derivatives, one cobalt ion and two coordinated water molecules, shown in Figure 1. The central cobalt ion adapts highly-distorted octahedral configuration and is coordinated by two carboxylate oxygen atoms from benzoate and amino acid, two aqua molecules and two N atoms from imidazole ring and amino N atom. One coordinated aqua molecule inter-links two adjacent cobalt atoms to form the dinuclear unit. The Co-N and -O bond distances range from 2.088(4) to 2.350(3) Å, in accordance with the Co(II) state. Each L ligand utilizes its part of amino acid to chelate one cobalt ion, which was further connected by the benzoate part of other derivative to form the 1D chain. The staggered 1D chains was cross-linked by coordinated aqua molecules to construct the 2D layer structure.

Electronic spectra of 1

Electronic spectra of phase-pure micro-crystal samples of **1** are also measured. The pink color of compound **1** is consistent with an octahedral environment of divalent cobalt. One absorption band centered at 226 nm could be assigned to n → π* transitions caused by ligand-centered electronic transitions; the other at 512 nm might be ascribed to $[^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)]$ transitions, in accord with the typical hexa-coordinated octahedral coordination environment of high spin Co(II) species.

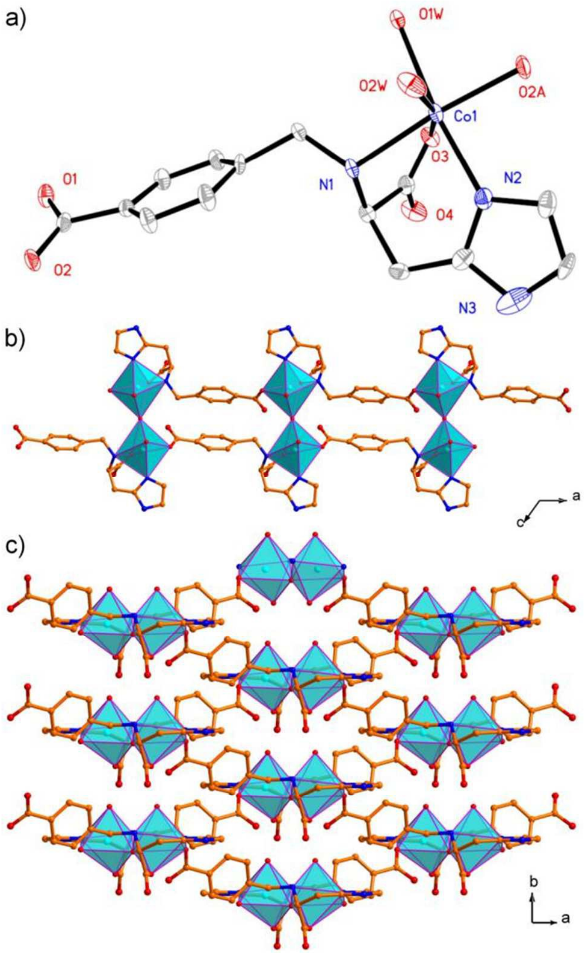

Figure 1. a) the asymmetric unit of **1**, hydrogen atoms were omitted for clarity; b) the perspective view of double-layered 2D structure of **1** along b-axis direction; c) the perspective view of double-layered 2D structure of **1** along c-axis direction.

Catalytic properties of 1 and 2

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As a test reaction for catalytic activity, the liquid-phase oxidation of cyclohexene in the presence of **1** and **2** was also examined using *tert*-butyl hydroperoxide as oxidant. Normally, cyclohexene oxide acted as the main product of the reaction of catalytic epoxidation was detected with the cobalt-based CPs as catalyzer. However, the different and interesting catalytic result was exhibited when **1** utilized as catalytic agent in the oxidations of cyclohexene. In contrast to other reports about the lesser extent of catalytic effect with respect to the Co-based CPs, the catalytic data demonstrates that oxidation of cyclohexene in the presence of **1** is fast, and several turnovers are possible in the presence of **1** (Figure 2), whereas the reaction occurring in the absence of catalyst under the same conditions is almost negligible (ca. 1% conversion after 6 h). The reaction was first tested on the oxidation reaction using *t*-BuOOH as oxidant at 60 °C, giving the maximum substrate conversion of 82.56% after 6 h. The main reaction product is *tert*-butyl-2-cyclohexenyl-1-peroxide (named as *P1*), followed by the by-product, 2-cyclohexen-1-one (named as *P2*) and cyclohexene oxide (named as *P3*), which were further validated by combined gas chromatographic and mass spectrometric product analysis. **1** has an exceptionally high selectivity toward the formation of *tert*-butyl-2-cyclohexenyl-1-peroxide (ca. 72%), which is relative higher than the homogeneous catalysis with cobalt(II)-based CPs when alkyl hydroperoxides are utilized as the oxidant. A further increase of reaction time to 12 h did not bring about higher conversion and more excellent selectivity. In terms of the crystal structure, the open Co(II) sites on the surfaces should be responsible for the excellent catalytic activity since no accessible void in the unit cell could be observed. In addition, the steric configuration along with the designed derivative and corresponding spacial conformation of **1** might play important roles in resulting different main product compared to other similar Co-based catalysts.[6a]

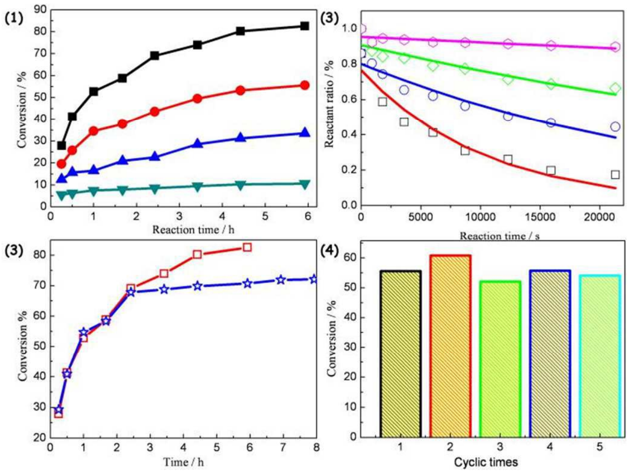

Figure 2. (1): Conversion versus time curves for cyclohexene oxidation with **1** as catalyst at 30 ℃(black), 40 ℃(red), 50 ℃ (blue) and 60 ℃(green); (2): Fitness of the conversion of cyclohexene at different temperature; (3)Allylic oxidation of cyclohexene with **1** as catalyst (square) and filtration of **1** (star) at 60 ℃;(4) Cyclic experiments utilized the same catalyst at 50 ℃. Reaction conditions: cyclohexene (10 mmol), t-BuOOH (18.5 mmol), 1,2,4-trichlorobenzene (1.5 mmol; as internal standard), 1 (0.0135 mmol, based on cobalt). TON = 435 , TON(turnover number) = moles converted/mol of active Co site. TOF = 0.138 h^{-1}.

To confirm the heterogeneous nature of the catalytic reaction, **1** was removed from the hot solution by filtration after reaching approximately 65% conversion (which took about **3** h for 1) at 60 ℃. It is clear from Figure 2 that no further catalytic conversion was observed, indicating that cobalt ions (if any) leaching from **1** are not responsible for the observed activity. The filtrate was also analyzed by atomic absorption spectroscopy (AAS), which indicated that no free cobalt(II) ions in the filtrate were detected due to the concentration of cobalt(II) ions beyond the lower detection limit of the AAS instrument. The results indicated that **1** behaves as a truly heterogeneous catalyst. More importantly, the catalyst could be easily retrieved and reused. The results of oxidation with the recycled catalyst in five times exhibit the similar efficiency, which indicated reusable and efficiently catalytic activity of **1**, even with little higher catalytic result of the second time that might be caused by the error in operation.

To further investigate the quick catalytic reaction, the chemical kinetics including the rate constant and activity energy was determined. The rate constant (*k*) for these reactions, which was utilized to calculate the activation energy, was determined at different temperatures (30, 40, 50 and 60 °C), as shown in Figure 2. The conversion in the presence of **1** increased with the reaction temperature from 30 to 60 °C, along with the increasing of rate constant (listed in Table 2). The increasing trend of rate constant (*k*) for the conversion of cyclohexene indicates that the oxidation of cyclohexene was an energy-activated process. According to the Arrhenius equation, the plot of ln *k* versus T^{-1} gave an activation energy (E_a) in units of kJ·mol^{-1}. The energy of activation for the oxidation of cylcohexene in the presence of **1** was finally approximately calculated as 91.98 kJ mol^{-1}, which are well validated that **1** as catalyst plays an important role in decreasing the energy of activation and promote the corresponding reaction quickly.

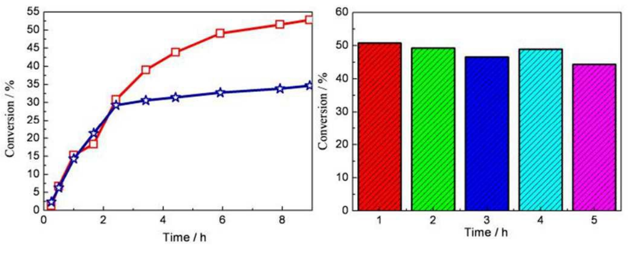

Figure 3. (left) Allylic oxidation of cyclohexene with **2** as catalyst (square) and filtration of **2** (star) at 60 ℃; (right) Cyclic experiments utilized the same catalyst at 60 ℃. Reaction conditions: cyclohexene (10 mmol), *t*-BuOOH (18.5 mmol), 1,2,4-trichlorobenzene (1.5 mmol; as internal standard), 1 (0.0135 mmol, based on manganese).

Comparably, substituted **1** catalyst with catalyst **2**, much lower catalytic productivity had been presented at 60 °C, giving the maximum substrate conversion of 52.36% with the selectivity toward the formation of *tert*-butyl-2-cyclohexenyl-1-peroxide (ca. 75%) after 8 h, shown in Figure 3. No free

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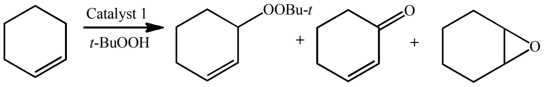
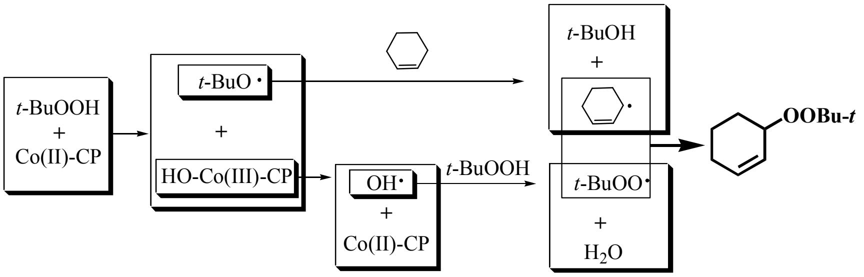
Mn(II) ions in the filtrate were detected due to the concentration of Mn(II) ions beyond the lower detection limit of the AAS instrument, which was also verified by the filtration experiment. The results indicated that **2** behaves as a truly heterogeneous catalyst. However, the catalytic effect of **2** is obviously not good as **1**, which might be ascribed to the natural advantage of cobalt ions compared to manganese ions. According to the assumed mechanism, the divalent catalyst would convert to trivalent one, and then recovery. The transition between Co(II) and Co(III) species seems easily compared to Mn catalyst due to the electronic configurations of spin state of different metal ions, which might be responsible for the difference of catalytic results. [15]

Table 2. Conversion and Kinetic Parameters at Optimum Molar Ratio of the Allylic Oxidation of Cyclohexene with 1 as Catalyst



Temp. (▯)	Total Con. (wt %)	*P1* Con. (wt %)	*P2* Con. (wt %)	*P3* Con. (wt %)	k (L mol^{-1} s^{-1})	E_a (kJ mol^{-1})
30	10.58	67.22	16.93	15.85	3.36×10^{-6}	91.98
40	33.51	62.8	17.59	19.61	1.73×10^{-5}	
50	55.58	73.94	14.50	11.56	3.60×10^{-5}	
60	82.56	71.93	15.23	12.84	9.94×10^{-5}	



Scheme 1. The proposed reaction mechanism of **1**-catalyzed allylic oxidation of cyclohexene

Oxidation Mechanism with 1 Catalyst.

With the consideration of tert-butyl-2-cyclohexenyl-1-peroxide as the main product and previous mechanistic studies of cobalt catalysis, a reaction pathway that freely diffusing peroxy radicals are generated by reductive cleavage of *tert*-butyl hydroperoxo coordinated onto cobalt(III) centers in CP had been set up.

In the initiation step, *t*-BuOOH ligands preferentially utilize an oxygen atom to coordinate onto the unoccupied coordination site of Lewis acid Co(II) ions in the assemble of **1**.[6a,9f] Electrons transfer from the Co(II) centers to the peroxy bond of *t*-BuOOH, causing the breakdown of weak O−O bonds, and bring out of *tert*-butoxy radicals (*t*-BuO·) and HO-Co(III) species. On the one hand, the resulting HO-Co(III) species might release the ·OH radical via fission of the Co−O bond,[10e] which would further react with *t*-BuOOH molecule to produce *t*-BuOO· radical. The HO-Co(III) species could recover the initial catalyst which could repeat the catalytic again. On the other hand, the resulting *t*-BuO· radical quickly draw a hydrogen ion from cyclohexene to yield 3-cyclohexenyl radical and *t*-BuOH. Then, the excess *t*-BuOO· radical continuously combine with 3-cyclohexenyl radical to result in *tert*-butyl-2-cyclohexenyl-1-peroxide.[10b] In addition, the O-O bond of *tert*-butyl-2-cyclohexenyl-1-peroxide is not stable and thermally decomposes to give the byproduct 2-cyclohexen-1-one.

Conclusions

In summary, we have succeeded in preparing a catalyst based on cobalt coordination complex containing histidine derivative through self-assembly under hydrothermal reaction conditions, which exhibits high catalytic effect for oxidizing cyclohexene to give allylic products under mild condition. The Co-based catalyst undergoes no metal leaching, and could be easily recovered from the catalytic reaction system. This research work highlights the potential of developing CPs as highly stable, molecularly tunable, recyclable and reusable heterogeneous catalysts for alkene oxidation, which would lead to commercial exploitation of Co-based CPs with the highly catalytic activity toward formation of oxygenated cyclohexene derivatives.

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Experimental Section

Materials and Methods. All reagents and solvents were purchased from commercial sources. The ligand was synthesized according the reference.[14a] FT-IR spectra were measured in the 4000–400 cm^{-1} range on a Mattson Alpha-Centauri spectrometer. Elemental analysis (C, H, N) was performed on a VarioEL III Elemental Analyzer. The catalytic products were measured by GC equipment with a capillary (30 m long × 0.25 mm i.d., WondaCAP 17) and FID detector (GC-2014C, Shimadzu, Japan). All UV/vis spectra were tested by a Cary TU-1900 double beam UV–vis spectrophotometer.

Synthesis of {(Co(L)(H$_2$O))$_2$(H$_2$O)}$_n$ (**1**). A mixture of $CoCl_2 \cdot 6H_2O$ (9.5mg, 0.04mmol), H_2L (8.8mg, 0.02mmol) were added to a solution of H_2O (4 mL) .The mixture solution was sealed in a Teflon-lined steel autoclave and the pH adjusted to about 7 with 2mol/L NaOH, then heat at 90 °C for 3 days. After it was cooled to room temperature and filtration, pink block crystals of **1** in a yield of 50.4% (based on L) were obtained. Anal. Calcd for $C_{28}H_{32}Co_2N_6O_{11}$: C, 45.05; H, 4.32; N, 11.26. Found: C, 44.69; H, 3.98; N, 11.62. IR (KBr pellet, cm^{-1}): 3377, 3231, 2924, 1606, 1532, 1397, 1311, 1081, 995.

Synthesis of {(Mn(L)(H$_2$O))$_2$(H$_2$O)}$_n$ (**2**). Similar synthesis method to 1, excepted for the metal salt as $MnCl_2$. Anal. Calcd for $C_{28}H_{32}Mn_2N_6O_{11}$: C, 45.54; H, 4.37; N, 11.38. Found: C, 45.03; H, 3.88; N, 11.93. IR (KBr pellet, cm^{-1}): 3372, 3230, 2924, 1606, 1531, 1396, 1310, 1082, 994.

X-Ray Structural Determination. X-ray diffraction data of **1** (0.2 × 0.1 × 0.1 mm) and **2** (0.2 × 0.2 × 0.1 mm) were collected on Bruker diffractometer using Mo-*Kα* (λ = 0.71073 Å) radiation at room temperature. The structures of complexes were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least squares procedure based on F^2 values. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. CCDC-1533551 (**1**) and CCDC-1533552 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Catalytic Oxidation of Cyclohexene. 1 or **2** was added to a solution of cyclohexene (10 mmol), *t*-BuOOH (18.5 mmol, 70% in water), 1,2,4-trichlorobenzene (1.5 mmol; as internal standard), catalyst (0.0135 mmol, based on metal ions) at room temperature.The reaction mixture was stirred at 60 °C. Aliquots of the reaction mixture (about 0.1 mL) were removed after time intervals indicated in the main text. Each sample was diluted with cyclohexane (1 mL) and filtered through a 0.25 mm Acrodisc nylon filter. Then, the sample was identified by GC–MS and quantified by GC. For investigations on metal leaching from the catalyst, the hot reaction mixture was filtered at the reaction temperature after 3 h. To investigate catalyst activities in subsequent multiple runs, the catalysts were separated from the reaction mixture by centrifugation and rinsed five times with cyclohexane before reuse. All yields and conversions were based on cyclohexene. The activation energy of catalytic experiments were carried out at different temperature under the same conditions as above description. And the catalytic results were fitted by NONLIN software by utilizing Arrhenius equation.

Acknowledgements

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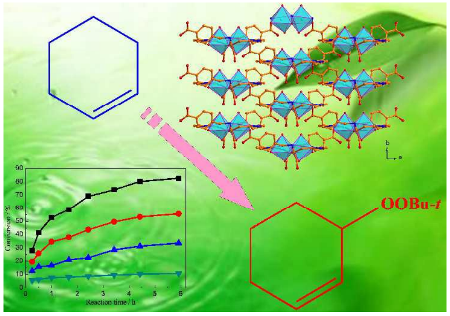
2D Co-based coordination polymer with histidine derivative as an efficient heterogeneous catalyst for the oxidation of cyclohexene



By utilizing the histidine derivatives acted as the organic linker, a 2D cobalt based coordination polymer had been constructed. The activated cobalt based heterogeneous catalyst shows highly catalytic activity in the allylic oxidation of cyclohexene and selectively catalyzes the oxidation reaction toward formation of *tert*-butyl-2-cyclohexenyl-1-peroxide.