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ARTICLE

A Highly Efficient Heterogeneous Catalyst of Cobalt-based Coordination Polymer For Aerobic Epoxidation of Cyclohexene

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Fan Yu[a,*]

Abstract: A novel heterogeneous catalyst of cobalt-based coordination polymer with tyrosine-based derivative had been successfully constructed. Heterogeneous catalytic experiments on allylic oxidation of cyclohexene indicate that titled complex present highly catalytic activity by utilizing the *tert*-butylhydroperoxide (t-BuOOH) as oxidant. The activation energy for the whole process of oxidation of cylcohexene had been calculated as 25.5 kJ mol^{-1}, which indicate the important role of the selected ancillary ligands in the resulted heterogeneous catalyst.

Introduction

Conversion of alkenes into value-increased oxygenated products is of a basic reaction in chemistry which has been widely used in the bulk chemical industry and fine chemicals.[1] Among the versatile alkenes, oxidation of cyclohexene is especially important and extensively investigated because its oxidation products are valuable intermediates. To some extent, traditional catalytic procedures produce a large number of environmentally undesirable wastes during the reaction process. And therefore, how to attain the effectively green reaction of catalytic oxidation of alkenes has been becoming imperious demands.[2]

It has been revealed that transitional metal complexes containing redox active transition metals are important homogenous catalysts which can selectively oxidize alkenes into the specific oxydate.[3] 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 level of environmental protection. Compared to homogeneous catalysts, the heterogeneous ones possess specific advantages, such as easy separation, efficient recycling and minimizing metal trace in the final product. However, the mechanism of the catalytic reaction between heterogeneous catalysts and catalytic reactions is very difficult to understand, and more systems are required to present the deep cognition of the catalytic process.

The research of Coordination Polymers (CPs) is undergoing an explosive growth stage since CPs would exhibit the diverse structures, known spatial configurations and specific sites for adsorbing the guest molecules[4,5], which has been also utilized as heterogeneous catalysts based on the several considerations: 1) the catalytically active sites could be easily implemented on the organic or the inorganic component of CPs via different easy-ways as heat or mechanic force[6]; 2) the separation and re-cyclic use of CPs based heterogeneous catalysts could be easily achieved since the stable topological structures of CPs[7]; 3) more importantly, CPs can explore the mechanism of catalytic reaction at the micro level, which helps us to further understand the subtle structural-activity relationship between catalyst and catalytic reaction[8]. In addition, as one unique advantage of CPs , the specific configuration and active sites could be finetuned via crystal engineering. The versatile choices of organic linkers would change the configuration and functionality of the final materials, which is very important for improving the anticipated properties. Therefore, more efficient, green and portable CPs-based catalysts are expected to boost the development of related research fields via crystal engineering.

Through the previous investigation, the advantages of catalyst must be originated from the coordination habits of cobalt center and amino acid derivatives. Referred to the related results, the adjustment of the final structures of CPs via using different amino acid derivatives should obviously modify the reaction pathway.[9] Therefore, to further explore the structural-activity relationship and catalytic mechanism of CPs-based catalyst, the new type of L-tyrosine-based derivative was adapted to adjust the corresponding catalytic effect guided by the results achieved in crystal engineering. Tyrosine, as one of the common amino acids, has shown widely attractive applications in many fields, but rarely in catalytic scope. Herein, a novel cobalt(II)-based CP,

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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.

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$\{[Co(H_2O)(L)_2)_2]\cdot(H_2O)\}_n$ (**1**, L = 3-(4-hydroxyphenyl)-2-(pyridin-4-ylmethylamino) propanoic acid), constructed by tyrosine-based derivative had been successfully synthesized, and then whose catalytic effect for oxidation of alkenes had been investigated.

Results and discussions

Crystal structure of 1

Crystal samples of **1** were synthesized by slow evaporation at room temperature, which were further characterized via single crystal X-ray diffraction, elemental analyses and IR spectrum (Figure S1). The existence of O-H, N-H and C-H groups could be deduced from the broad peaks of stretching vibrations around 3583-3532, 3445-3330 and 3103-2883 cm^{-1}. The asymmetric and symmetric stretching vibrations of deprotonated carboxyl could be also validated via the peaks around 1605 cm^{-1} and 1382 cm^{-1}. In addition, the existence of the pyridyl ring could be also verified via the stretching vibrations at 1665, 1570, 1560 and 1470 cm^{-1}. After heated, the typical IR peaks could be still observed in the spectra, indicating the reservation of specific function groups in activated sample.

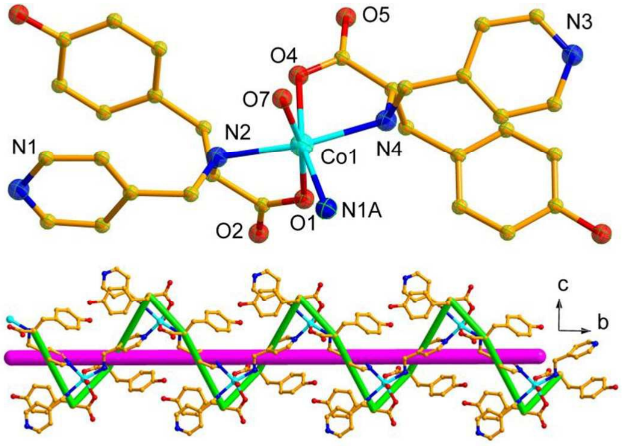

Fig. 1 Up: the view of asymmetric unit of **1**, hydrogen atoms were omitted for clarity. Asymmetric code: -X+2, Y+1/2, -Z+3/2; Down: The perspective view of 1D helical chain in **1**.

The investigation of crystal structure has been carried out at room temperature. Crystal data and selected structural parameters are listed in Table S1 and S2. Compound **1** crystallizes in the orthorhombic space group *P*2(1)2(1)2(1), whose asymmetric unit contains two tyrosine derivates, one cobalt ion and one coordinated water molecule (Figure 1). The central coblat ion adopts octahedral configuration and is coordinated by one pyridyl-N atom, two carboxylate oxygen atom, one aqua molecule and two aliphatic N atoms, while the axial positions are occupied by two oxygen atoms from water molecule and carboxylate group. Two adjacent de-protonated amino acid derivates utilize their N-O chelate mode to occupy the *cis*-coordination sites of center. The Co-N and -O bond distances range from 2.088(4) to 2.201(3) Å, in accordance with the Co(II) state.[10] In addition, the L ligand was folded caused by the weak π-π interaction (4.028 Å) between two aromatic rings (center-to-center). The adjacent cobalt centers were further interconnected by one of the amino acid derivate via the decorated pyridyl-N atom (N1) to form the 1D helical chain along *b*-axial direction. Each 1D chain binds onto adjacent ones through hydrogen bonding interaction to assemble the 3D supramolecular network. Viewed from the packing mode, the hydroxyl of phenol and coordinated water molecule locate toward the outside of chain structure, which might be useful to improve its catalytic ability referred to other CPs acted as heterogeneous catalysts. In addition, the existence of hexa-coordinated Co(II) state in **1** could be also validated by the absorption peaks around 510 nm in UV-Vis (Figure S2) for the crystal samples[10].

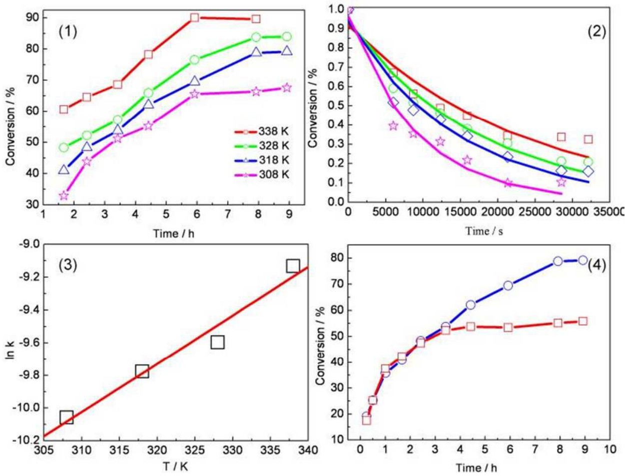

Fig. 2 (1): Conversion *vs*. Reaction time curves for the oxidation of cyclohexene in the presence of **1** as catalyst at 35 ⍰, 45 ⍰, 55 ⍰ and 65 ⍰; (2): Simulation of the conversion curves at different temperature; (3) Simulation of ln*k* *vs*. temperature; (4) Allylic oxidation of cyclohexene with **1** as catalyst (circle) and filtration of **1** (square) at 55 ⍰. Reaction conditions: cyclohexene (12 mmol), *t*-BuOOH (18.5 mmol), 1,2,4-trichlorobenzene (1.5 mmol; as internal standard), 1 (0.075 mmol, based on cobalt).TON equal to 546, TON (turnover number) = moles converted/mol of active Co site. TOF= 0.078 h^{-1}.

Catalytic properties of 1

The purity of as-synthesized crystal samples had been examined by PXRD, which presents the anticipated consistency with simulated spectra from crystal structure (Figure S3). The minor difference between the simulated and experimental patterns might be caused by the guest molecules in the lattice, which was not fixed via the studies of X-ray diffraction. Therefore, the activated samples obtained from the as-synthesized crystal samples were directly utilized for catalytic oxidation of cyclohexene with the oxidant of *tert*-butyl hydroperoxide. When most of the reported cobalt CPs acted as the catalyst in the oxidation of cyclohexene, 2-cyclohexen-1-one is usually detected as the main product, and the extent of catalytic effect is also not exciting. However, an exhilarating catalytic effect could be achieved with the presence of **1** as the catalyzer in the oxidation of cyclohexene, including not only the different main product, but also the very fast reaction

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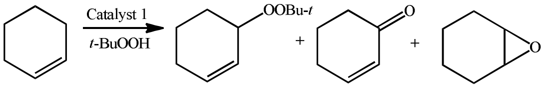
velocity. The catalytic results had been gathered in Table 1. When the oxidation reaction was firstly monitored under the routine conditions but without the the titled catalyst for twelve hours at 65 °C, no obvious catalytic result could be detected. Comparably, a very significant catalytic result could be achieved after five hours under the same conditions in the presence of **1** as the catalyst. The maximum substrate conversion of 93 % could be given. Through the analysis by gas chromatographic and mass spectrometric, the main product is *tert*-butyl-2-cyclohexenyl-1-peroxide (*P1*), while the by-products are 2-cyclohexen-1-one (*P2*) and cyclohexene oxide (*P3*). In addition, compared to the usual catalytic reaction with homogeneous catalyst based on cobalt CPs and the oxidant of alkyl hydroperoxides, the selectivity for *P*1 is also very high, and calculated as 83% at 65 °C (Table 1). Thus high selectivity is higher than the reported heterogeneous catalysis with the cobalt(II) complexes as catalyst, and manifest the specific advantage of complex 1 as the heterogeneous catalyst.[9,10] No additional increases of conversion and selectivity could be detected since the reaction time prolongated to twelve hours. In the previous work, it had been concluded that even without obvious porous structure, the open metal sites on the surfaces should be also assigned to the corresponding catalytic results. Herein, for **1**, the open cobalt sites are more directly exposed to the periphery due to the twistable chain-like structure. The more open configuration could ensure the smaller spacial hindrance effect, and might be beneficial for the combination of cobalt center and hydroxyl radical for **1**, which subsequently promises the excellent catalytic results.

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

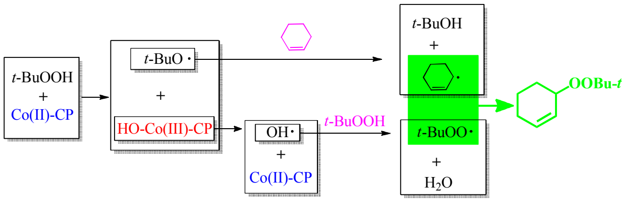


Temp. (⍰)	Total Con. (wt %)	*P1* Con. (wt %)	*P2* Con. (wt %)	*P3* Con. (wt %)	k (L mol-1 s-1)	Ea (Kj mol-1)
35	67.58	77.22	10.93	11.85	4.28×10-5	25.5
45	79.16	86.69	6.88	6.43	5.68×10-5	
55	83.98	84.71	7.04	8.25	6.80×10-5	
65	89.62	82.97	6.27	10.76	1.08×10-4	

The role of heterogeneous catalyst of **1** could be confirmed by two additional experiments. Firstly, as shown in Figure 2, no further catalytic conversion could be detected after removing the solid catalysts from the hot reaction solution since the reaction occurred for 3h. Secondly, no cobalt(II) ions could be detected from the analysis of atomic absorption spectroscopy (AAS), indicating the concentration of cobalt(II) ions in the resulted filtrate was lower than the limitation of the corresponding equipment. All of these two experiments illustrate that rare cobalt ions leach from the solid catalyst. And even there are some cobalt ions infiltrating into the reaction solution, they would not be responsible for the catalytic results. Therefore, the titled complex could truly act as the heterogeneous catalyst for oxidation of cyclohexene. In addition, the cyclic test verified the reusable catalytic activity with negligible loss of efficiency.

To present the deep cognition for the catalytic activity of **1**, the related chemical kinetics, the rate constant and activity energy, were further calculated. The catalytic experiments with the same conditions have been further carried out at 35, 45 and 55 °C (Figure 2), which exhibit the excellent catalytic results even at 35 °C with the maximum conversion of 65% after 5 h. The rate constants simulated from the experimental curve exhibit the increasing tendency along with the increase of reaction temperature, indicating the energy-activated process for the oxidation of cyclohexene. The corresponding activation energy (E_a) for the the oxidation of cylcohexene with the catalyst of **1** was finally determined as 25.5 kJ mol^{-1} according to Arrhenius equation (Figure 2). Compared to other reported E_a values of cobalt-based catalysts, the parameters for **1** was very small, validating the vital role in promoting the process of related catalytic reaction.[9,10]

The selectivity of **1** to the above description catalytic reaction had been further explored by substituting the substrate of cyclohexene with styrene, and different catalytic results have been presented. Although with the same reaction conditions, styrene oxide as the main production had been examined. The catalytic reaction was also carried out at 65 °C for eleven hours, presenting the maximum conversion of 55% (Figure S10). However, the main reaction product is ascribed to styrene oxide, while the by-product is benzaldehyde with a very small amount. The different catalytic results for different substrates manifests that the titled complex as heterogeneous catalyst for olefin compounds has definite selectivity toward different substrates.



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

Oxidation Mechanism with 1 Catalyst.

By utilizing the 1 as heterogeneous catalysts, the main production is *tert*-butyl-2-cyclohexenyl-1-peroxide. With the consideration of final product and cobalt-based catalyst, the mechanism of reaction pathway had been proposed as scheme 1. The diffusing peroxy radicals are firstly produced via the reductive cleavage of *t*-BuOOH that coordinate onto cobalt(III) centers in CP, and then induce the series of reaction.

Initially, *t*-BuOOH molecules preferentially coordinate onto cobalt centers by the utilization of oxygen atom, and occupy the remnant Lewis acid site of cobalt centers.[9,11] And then, *tert*-butoxy radicals (*t*-BuO·) and HO-Co(III) matter tend to be released due to the the breakdown of weak O–O bonds of *tert*-

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butyl hydroperoxide, caused by charge transfer from the Co(II) ions to the peroxy bond. The produced HO-Co(III) matter would release the hydroxyl radicals and become the initial state due to the breakdown of Co–O bond, which is beneficial for the production of *t*-BuOO· radical. Meanwhile, the hydrogen atom on cyclohexene would be easily drawn by the *tert*-butoxy radicals (*t*-BuO·) , and produce the 3-cyclohexenyl radical and *t*-BuOH. The resulted 3-cyclohexenyl radical could combine the excess *t*-BuOO· radical to produce the main product of *tert*-butyl-2-cyclohexenyl-1-peroxide, which could result the by-product of 2-cyclohexen-1-one due to the thermal decomposition. Therefore, with the consideration of the postulated reaction mechanism in the related previous results, the first step is the combination of cobalt centers and hydroxyl radicals originated from the alkyl hydroperoxides, which might be of the rate-determining step in the whole catalytic cycle.[9,11] The open metal sites of the helical chain are very beneficial for the binding of the hydroxyl, and then accelerate the corresponding steps to the final product. The specific helical configuration and more open metal centers might be of the important features of **1** as the heterogeneous catalyst to cyclohexene, and reflect the specificity of the catalytic reaction.

Conclusions

In conclusion, by utilizing the tyrosine-based derivative and cobalt ions as the components of CP, a new type of highly efficient heterogeneous catalyst for the oxidation of cyclohexene have been successfully constructed, whose detailed catalytic activity including activation energy, selectivity, cyclic performances and versatile reaction parameters had been investigated. By means of microscopic structural analysis, we can understand the vital influence of the spatial configuration of complexes on the final catalytic effect, which further emphasize the important role of crystal engineering in adjusting the the desired functionality of final materials. In the future, more similar CPs-based catalysts with excellent catalytic activity are desired to promote the development in the field of heterogeneous catalysts.

Acknowledgements

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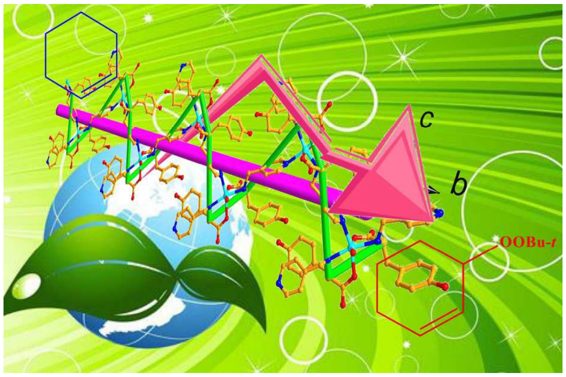

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