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Allylic oxidation of olefins with a manganese-based metal-organic framework

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Abstract: Selective oxidation of olefins to α,β -unsaturated ketones under mild reaction conditions have attracted considerable interest, since α,β -unsaturated ketones can serve to be synthetic precursors for various downstream chemical products. The major challenges inherently with this

chemical oxidation are chem-, regio-selectivity as well as environmental concerns, i.e. catalyst recycle, safety and cost. Using atmospheric oxygen as an environmental friendly oxidant, we found that a metal-organic framework (MOF) constructed with Mn and tetrazolate ligand (CPF-5) showed good activity and selectivity for the allylic oxidation of olefins to α,β -unsaturated ketones. Under the optimized condition, we could achieve 98% conversion of cyclohexene and 87% selectivity toward cyclohexanone. The combination of a substoichiometric amount of TBHP (*tert*-butylhydroperoxide) and oxygen not only provides a cost effective oxidation system but significantly enhances the selectivity to α,β -unsaturated ketones, outperforming most reported oxidation methods. This catalytic system is heterogeneous in nature, and CPF-5 could be reused at least five times without a significant decrease in its catalytic activity and selectivity.

1. Introduction

Selective oxidation of olefins at allylic positions is an important synthetic route to α,β -unsaturated ketones,^{1,2} which are valuable intermediates for the synthesis of fine chemicals,^{3,4} such as anticoagulant,⁵ antiviral and cytotoxic agents.⁶ As a consequence, a plethora of methodologies has been reported for this transformation. Stoichiometric oxidants (MnO_2 , KMnO_4 , CrO_3 , SeO_2 , peracetic acid, *m*-chloroperbenzoic acid and HNO_3) were commonly used oxidants.^{3,7,8} However, large amounts of hazardous pollutants were formed during the synthetic process, which makes these processes environmentally unfriendly. A stoichiometric amount of peroxides, i.e. *tert*-butylhydroperoxide (TBHP) or hydrogen peroxide (H_2O_2) were often employed as cleaner

replacement of the above chemical oxidants,⁹ but the cost and potential explosion factors restrict their further utilization. Moreover, most of the currently used oxidation methodologies are often encountered with the simultaneous generation of by-products, such as epoxides, enols, and diols.¹⁰ Therefore, selective oxidation of allylic C-H of olefins with molecular oxygen would be an ideal system for the access of α,β -unsaturated ketones.^{11,12}

Noble metals-based complexes (e.g., Pd, Pt, and Au) in combination with molecular oxygen are frequently employed for the allylic oxidation of alkenes.¹¹⁻¹⁸ As alternative non-noble metal-based catalysts, the first-row transition metals (e.g., Cr, Mn, Fe, Ni, and Cu) have been used in these oxidation reactions.^{10,19} Pioneering work on Mn/nitrogen containing ligand complexes catalyzed oxidation reactions has been reported by Jacobsen,²⁰⁻²³ Que^{24,25} and Costas²⁶⁻³² in both homogeneous and heterogeneous way, and those catalytic systems demonstrated considerably high TON for the oxidation of alkenes. Meanwhile, Mn Schiff base complexes are the most commonly used active homogeneous catalysts for the oxidation of olefins.³³⁻³⁵ However, the poor reusability of homogeneous catalysts increases the cost of the process, especially at a large scale. To address the reusability issue of homogeneous Mn catalysts, heterogeneous Mn-based catalysts have been developed using different supports, such as metal-organic frameworks (MOFs), mesoporous silica, zeolite and carbon materials.³⁶⁻⁴¹ MOFs are a class of crystalline materials, which can be constructed with different metal ions/cluster with various types of organic ligands.⁴²⁻⁴⁵ MOFs have been used to catalyze the oxidation of alkenes.^{46,47} However, there are many problems that restrict their broad applications, such as low selectivity,⁴⁸ the requirement of a stoichiometric amount of

oxidants like TBHP,^{49,50} and the use of high-pressure oxygen.⁵¹⁻⁵³ Therefore, developing highly efficient and low-cost heterogeneous catalysts for the selective oxidation of olefins with an ambient pressure of O₂ under mild reaction conditions is highly desirable.

Herein, we report an efficient catalytic allylic oxidation of olefins using molecular O₂ together with substoichiometric amount of TBHP as the co-oxidant under mild reaction conditions. Inspired by the chelated Mn sites with N/O-containing ligands that show superior activity,⁵⁴⁻⁵⁸ we choose a Mn-based MOF (CPF-5) with ligands containing both carboxylate and tetrazole groups as the heterogeneous catalyst for the oxidation reaction. CPF-5 was constructed with Mn and 4-tetrazole benzoic acid (4-TBA) ligands with formula [Mn₅(TBA)₃(HCOO)₃(OH)(H₂O)₂]₄·6DMF.⁵⁹ CPF-5 possesses large pores constructed by super-supertetrahedral SBUs (secondary building units). Each SBU contains five Mn ions with one tripodal unsaturated Mn site that can work as the active center for oxidation reactions. In this study, we found that CPF-5 is capable of catalyzing the oxidation of cyclohexene to cyclohexenone (2-cyclohexene-1-one) with molecular oxygen (1 bar) and TBHP (0.25 equiv.) as the oxidant under mild reaction conditions. CPF-5 was stable during the reaction process and could be reused at least five times without significant decrease in catalytic activity, which demonstrates its potential applications in the liquid-phase oxidation of olefins for the production of important fine chemicals.

2. Experimental section

2.1 Preparation of CPF-5

CPF-5 was prepared according to a modified method described in the literature.^{59,60} Manganese

chloride tetrahydrate (156 mg, 0.79 mmol), 4-tetrazole benzoic acid (4-TBA, 80 mg, 0.42 mmol) and ammonium formate (15 mg, 0.24 mmol) were dissolved in a mixture of 2 mL *N,N*-Dimethylformamide (DMF) and 0.2 mL water in a scintillation vial (24 mL). After dissolving all the chemicals by sonication, the mixture was placed in a 120 °C oven for 3 d. The resulted colorless crystals were separated by filtration while the mother liquid still warm to avoid the formation of amorphous precipitates. The crystals were washed with DMF (3 × 2 mL). The as-synthesized CPF-5 was immersed in acetonitrile (5 mL) at room temperature, then the solvent was decanted out after 12 h. Fresh acetonitrile was added and the above procedure was repeated for 3 times. The solid was activated under vacuum at 70 °C for 24 h.

2.2 Allylic oxidation of olefins

The allylic oxidation of olefins was carried out in a round bottom flask (10 mL) with a condenser attached. Generally, olefins (0.2 mmol), CPF-5 (5 mg), acetonitrile (1 mL), mesitylene (3 µL, as internal standard) and various amount of TBHP (0.25 - 2 equiv.) were introduced into the flask equipped with an oxygen balloon. The mixture was stirred at 60 °C, aliquots of the reaction mixture were taken out and diluted with acetonitrile and the solid catalysts were removed by centrifugation. The conversion of olefins was determined by a gas chromatograph (GC) equipped with a flame ionization detector (FID).

3. Results and discussion

3.1 Characterization of CPF-5

The powder X-ray diffraction (PXRD) pattern of the prepared CFP-5 matches with the

simulated patterns (Figure 1A). The strong IR band at 1678 cm^{-1} could be attributed to the stretching vibration of -C=O , which shifts to low frequency and stacks with other peaks after the formation of CPF-5 crystal (Figure 1B). The peaks at 1631 , 1572 and 1435 cm^{-1} represent -N=C , -N=N and -N-N stretching vibration (tetrazole ring), respectively. CPF-5 displays a type IV isotherm, a hysteresis loop is observed in the high relative pressure region (Figure 1C). The BET surface area is calculated to be $267\text{ m}^2\cdot\text{g}^{-1}$.

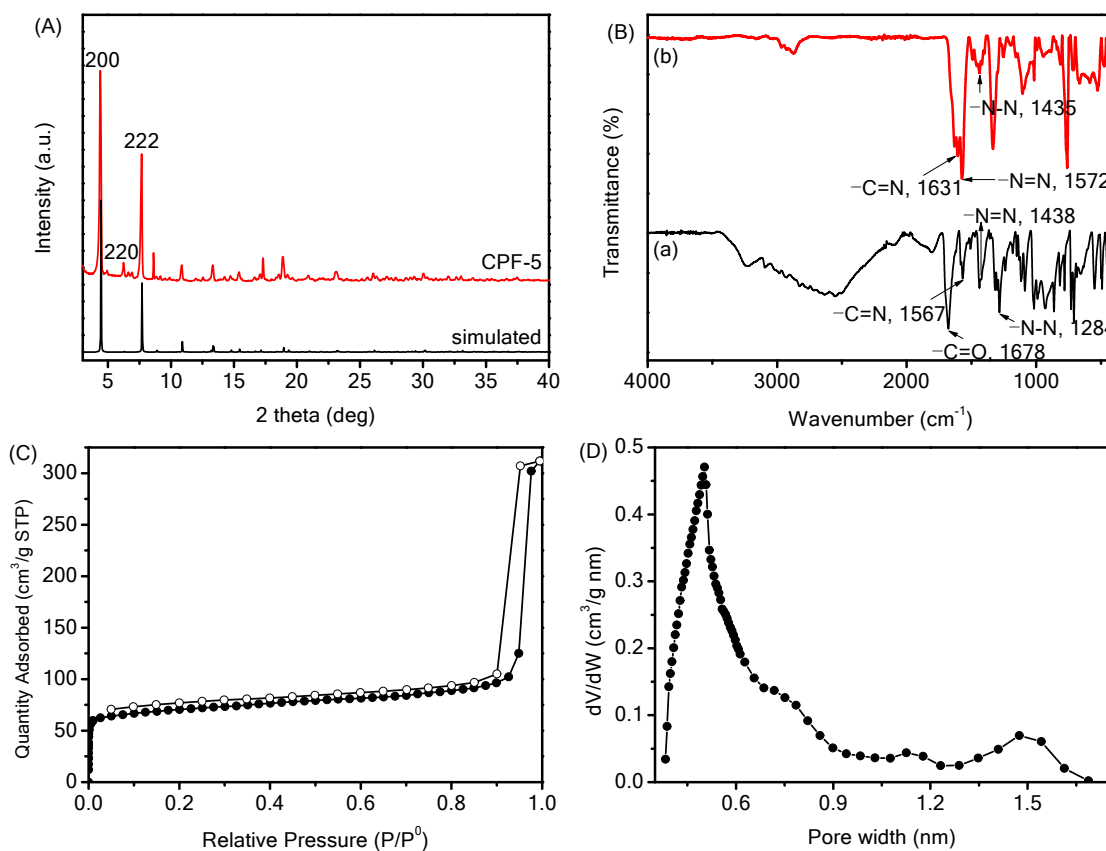


Figure 1. (A) Simulated and measured PXRD patterns of CPF-5. (B) FT-IR spectra of (a) organic linker 4-TBA and (b) CPF-5. (C) N_2 -sorption isotherm and (D) pore size distribution of CPF-5.

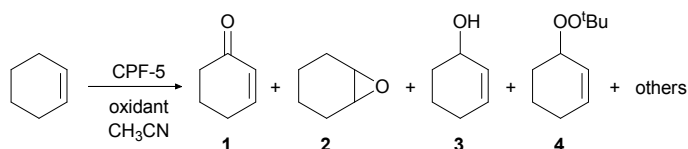
3.2. Catalytic activity studies

The oxidation of cyclohexene was used as a model reaction to evaluate the catalytic property of CPF-5 (Table 1). We first tested the solvent effect on the oxidation reaction in acetonitrile, DMF, or CHCl_3 . As shown in Figure S4, we could achieve 83% cyclohexene conversion and 60% selectivity to cyclohexenone in acetonitrile before we perform any optimization of reaction conditions. DMF gives both low activity and selectivity. We did achieve >90% conversion of cyclohexene in CHCl_3 , but the selectivity to the ketone is only 25%. Considering both conversion and selectivity, we chose acetonitrile as the solvent for further studies.

In the absence of CPF-5, only a small amount of cyclohexene was converted (Table 1, entry 1). We then tested the effect of different oxidants on the oxidation of cyclohexene. Moderate conversion of cyclohexene and medium selectivity to cyclohexenone is obtained with 2 equiv. of TBHP, affording higher TON (Table 1, entry 2) as compared with other oxidants. With ambient pressure oxygen only (Table 1, entry 3), we obtained 16% conversion of cyclohexene and 77% selectivity to cyclohexenone. Using hydrogen peroxide (H_2O_2) instead of TBHP, both the conversion and selectivity toward α,β -unsaturated ketone decreased to 22% (Table 1, entry 4). Using TBHP at the increased reaction temperature (40 °C) can facilitate the conversion of cyclohexene (86%) while keeping >40% selectivity to cyclohexenone (Table 1, entry 5). Interestingly, using 1 bar O_2 with 0.5 equiv. TBHP, we could achieve 80% cyclohexene conversion and 78% selectivity to cyclohexanone (Table 1, entry 6). Small amount of TBHP in the reaction mixture works as a radical initiator to trigger the oxidation reaction. It may cause the change of

Mn valence state and oxidation ability of CPF-5. Then CPF-5 can use the abundant oxygen molecules for the oxidation reaction, which can contribute to the high selectivity of the product.

Table 1 The oxidation of cyclohexene catalyzed by CPF-5.^a







Entry	Oxidant	T (°C)	Conversion (%)	TON	Selectivity (%)			
					1	2	3	4
1 ^b	TBHP	23	11	-	6	7	8	65
2	TBHP	23	57	29	42	4	5	44
3	O ₂	23	16	8	77	6	17	-
4	H ₂ O ₂	23	22	11	22	26	31	21
5	TBHP	40	86	44	46	3	30	9
6 ^c	TBHP + O ₂	40	80	40	78	1	4	2

^a Reaction conditions: cyclohexene (0.2 mmol), CPF-5 (5 mg, 0.004 mmol based on Mn₅ SBU), TBHP (2 equiv.), CH₃CN (1 mL), 24 h. ^b Without catalyst. ^c 0.5 equiv. TBHP and 1 bar O₂.

We then further decreased the amount of TBHP to 0.25 equiv. in the presence of 1 bar O₂ and observed similar cyclohexene conversion and cyclohexenone selectivity (Table 2, entry 1) as the 0.5 equiv. case. However, further decrease TBHP to 0.1 equiv. (Table 2, entry 2) slightly decreased the conversion. Increasing the reaction temperature to 60 °C, we could further enhance the conversion of cyclohexene and maintain >80% selectivity to the ketone product (Table 2, entries

3-5). With atmospheric O₂ and 0.25 equiv. of TBHP at 60 °C, we could achieve 98% conversion of cyclohexene and 87% selectivity toward cyclohexenone (Table 2, entry 3). Doubling the catalyst loading from 5 mg (Table 2, entry 4) has little effect on the conversion and selectivity, but 2.5 mg catalyst leads to an obvious decrease in both conversion and selectivity (Table 2, entry 5). Hence, the optimized reaction conditions are 0.2 mmol cyclohexene and 5 mg of CPF-5 in 1 mL of acetonitrile under 1 bar of O₂ with 0.25 equiv. of TBHP at 60 °C for 24 h.

Table 2 Optimization of the reaction conditions for CPF-5 catalyzed oxidation of cyclohexene.

Entry	T(°C)	Catalyst (mg)	TBHP (equiv.)	Conversion (%)	Selectivity (%)			
								
1	40	5	0.25	83	77	4	6	2
2	40	5	0.1	76	83	4	8	2
3	60	5	0.25	98	87	1	4	4
4	60	10	0.25	99	89	2	4	3
5	60	2.5	0.25	85	82	6	3	2

Reaction conditions: cyclohexene (0.2 mmol), CPF-5, TBHP, CH₃CN (1 mL), O₂ (1 bar), 24 h.

Under the optimized reaction conditions, we studied the reaction kinetics and product distribution over time (Figure 2). The cyclohexenone selectivity increases as the reaction time prolongs. 2-cyclohexene-1-ol (**3**) is formed simultaneously and reaches the highest amount at 1 h. Then its amount decreases and only 2.7% of **3** exists in the oxidation products mixture after 21 h. Hence, we speculate that the by-product 2-cyclohexene-1-ol can be further oxidized to

cyclohexenone. The amount of epoxide **2** keeps at a low level throughout the whole process, indicating that the oxidation of C=C is suppressed in this catalytic system. We also observed a trace amount of peroxide **4** (*tert*-butyl-2-cyclohexenyl-1-peroxide). As displays in Figure 2, the highest selectivity (87%) of cyclohexenone is achieved at 21 h. The allylic oxidation products are formed with high selectivity (~90%) with 3% of epoxide, it could cause by the reaction proceeds *via* a radical pathway. To verify the radical pathway, 3 equiv. of 2,6-di-*tert*-butyl-4-methylphenol (BHT, as a radical inhibitor) was added to the reaction mixture and the oxidation reaction was inhibited entirely (Table S1).

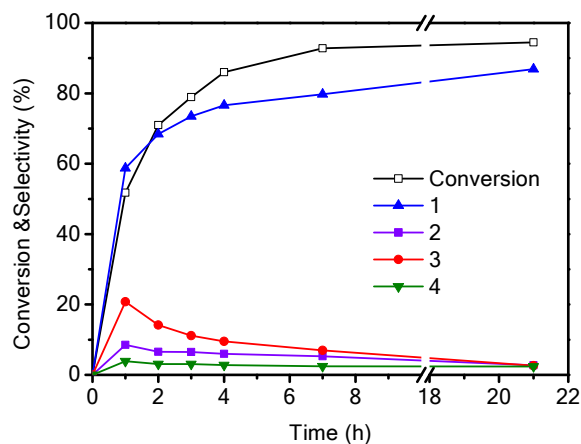
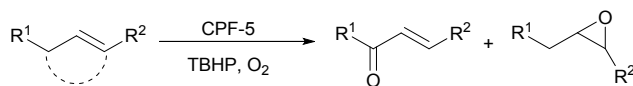


Figure 2. Time-conversion plot of cyclohexene catalyzed by CPF-5. Reaction conditions: cyclohexene (0.2 mmol), CPF-5 (5 mg), TBHP (0.25 equiv.), CH₃CN (1 mL), 60 °C, O₂ (1 bar).

We also compared the activity and selectivity of CPF-5 with other manganese salts in the oxidation of cyclohexene (Table S2). CPF-5 (Table S2, entry 1) gives 16% conversion of cyclohexene and 53% selectivity to α,β -unsaturated ketone, while less than 7% conversion of

cyclohexene was achieved with manganese salts as catalysts (Table S2, entries 2-4). The enhanced activity of CPF-5 could be originated from the special coordination environment of Mn in the MOF. It is worth to emphasize that the conversion and selectivity of the oxidation reaction catalyzed by CPF-5 (Table 2, entry 3) is among the top level as compared to those reported MOFs catalysts (Table S6), and relatively mild reaction conditions are used here.

To test the versatility of CPF-5, other olefins were used as substrates in these catalytic oxidation reactions (Table 3). For cyclic olefins (Table 3, entries 1-4), high conversion is achieved with α,β -unsaturated ketones as the major product. However, *cis*-cyclooctene (Table 3, entry 3) is an exception, medium conversion (62%) is achieved at 24 h and the main product is epoxide instead of the allylic oxidation product. The decreased conversion could be ascribed to the large molecule size of *cis*-cyclooctene that could restrict its diffusion. The selective generation of epoxide could be explained by a conformation effect⁶¹, where the allylic C-H bonds of *cis*-cyclooctene are almost orthogonal and hard to be reached. This conformation could facilitate the formation of epoxide. The oxidation of chain olefin (Table 3, entry 5) is not as efficient as that of cyclic olefins. Ethylbenzene can be oxidized at 80 °C, affording 31% conversion and 95% acetophenone selectivity (Table 3, entry 6). For substrate without allylic C-H bond (i.e. styrene), benzaldehyde is formed as the major product with 85% selectivity (Table 3, entry 7). Increase the amount of TBHP to 1 and 2 equiv. can improve the conversion of styrene but sacrifice benzaldehyde selectivity (Table 3, entries 8 and 9).

Table 3 CPF-5 catalyzed oxidation of different substrates.^a

Entry	Substrate	T (°C)	Conversion (%)	Product	Selectivity (%)
1		60	98		87
2		60	83		66
3 ^b		60	62		76
4		60	93		52
5		60	12		65
6 ^b		80	31		95
7		80	48		85
8 ^c		80	65		58
9 ^d		80	99		35

^a Reaction conditions: cyclohexene (0.2 mmol), CPF-5 (5 mg, 0.004 mol based on Mn₅ SBU), TBHP (0.25 equiv.), mesitylene (3 μL), CH₃CN (1 mL), O₂ (1 bar), 24 h. ^b 1.2 equiv. of TBHP. ^c 1.0 equiv. of TBHP. ^d 2.0 equiv. of TBHP.

In order to scale-up the reaction, one milliliter of cyclohexene was catalyzed by 20 mg of CPF-5 under a solvent-free condition with oxygen as the only oxidant. After reacted 24 h at 60 °C, 95%

cyclohexene conversion is achieved, which is accompanied with 62% cyclohexenone and 20% 2-cyclohexen-1-ol selectivity.

3.3 Reusability of the catalyst

The stability and recyclability of CPF-5 were tested with the recovered catalyst for several consecutive runs (Figure 3 and Figure S6). After 5 cycles, the CPF-5 could still afford 95% conversion and 70% cyclohexenone selectivity. The PXRD pattern of reused CPF-5 does show all the major diffraction peaks in comparison to the fresh one, but the peak intensity decreases (Figure S7), indicating the partial degradation of CPF-5.

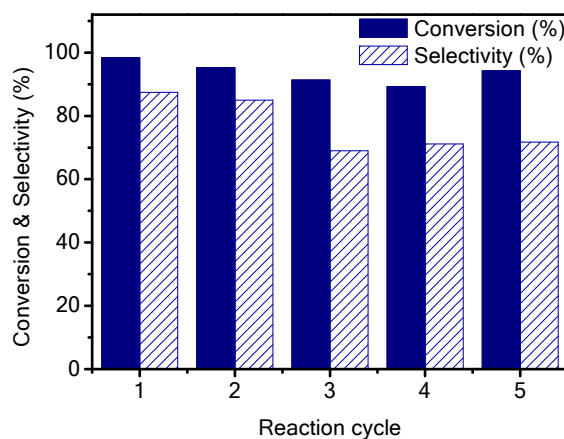


Figure 3. Recyclability test of CPF-5 in catalyzing the oxidation of cyclohexene. Reaction conditions: cyclohexene (0.2 mmol), CPF-5 (5 mg), TBHP (0.25 equiv.), CH₃CN (1 mL), 60 °C, O₂ (1 bar), 24 h.

To get some insights into the oxidation state of Mn in CPF-5, the fresh and reused catalysts were analyzed by XPS (Figure 4), the survey spectra show the peaks of Mn, O, N and C elements.

As shown in Figure 4c and 4d, the Mn $2p_{3/2}$ peaks with binding energies of 642.5, 641.4 and 640.4 eV correspond to Mn^{IV}, Mn^{III} and Mn^{II} ions, respectively. The fitted Mn $2p_{3/2}$ XPS spectra indicate that higher content of high valence Mn exists in the reused CPF-5 (44.7% of Mn^{IV}) as compared with the fresh one (33.3% of Mn^{IV}) (Table S3). The N 1s peak at 400.9 eV is originated from the positively charged N atoms due to the bonding of tetrazole ligand with manganese ions. Unlike the changes observed for Mn, the relative ratio of other elements almost keeps unchanged after the reaction (Table S4), which demonstrates the good stability of CPF-5 during the oxidation reaction.

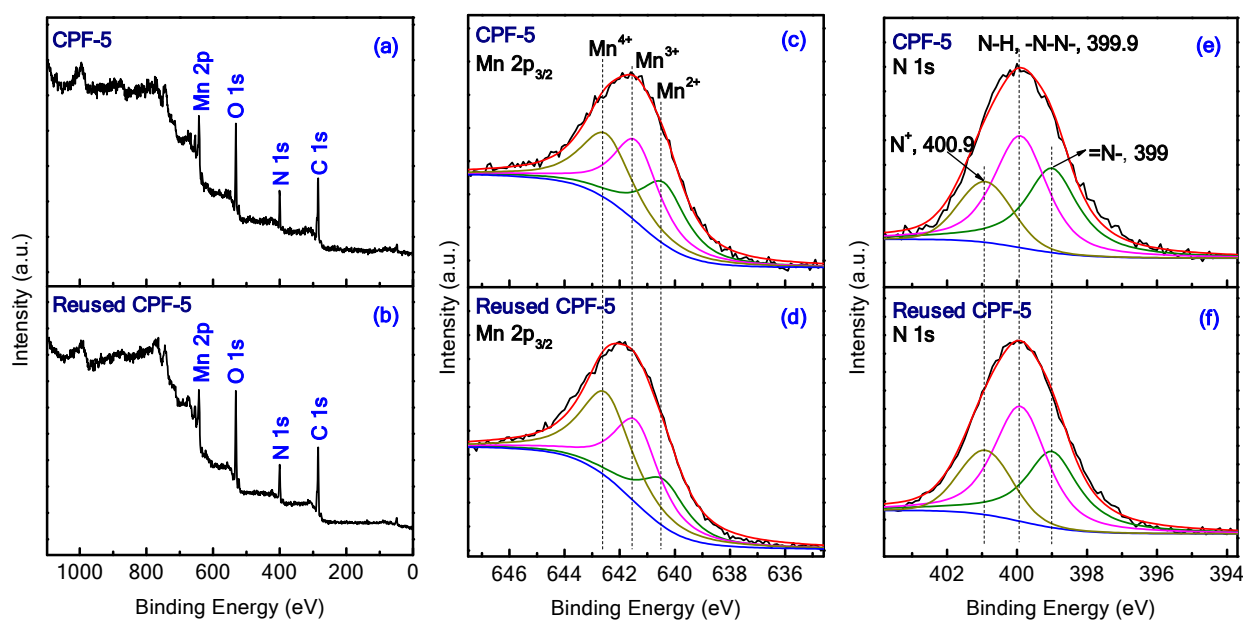
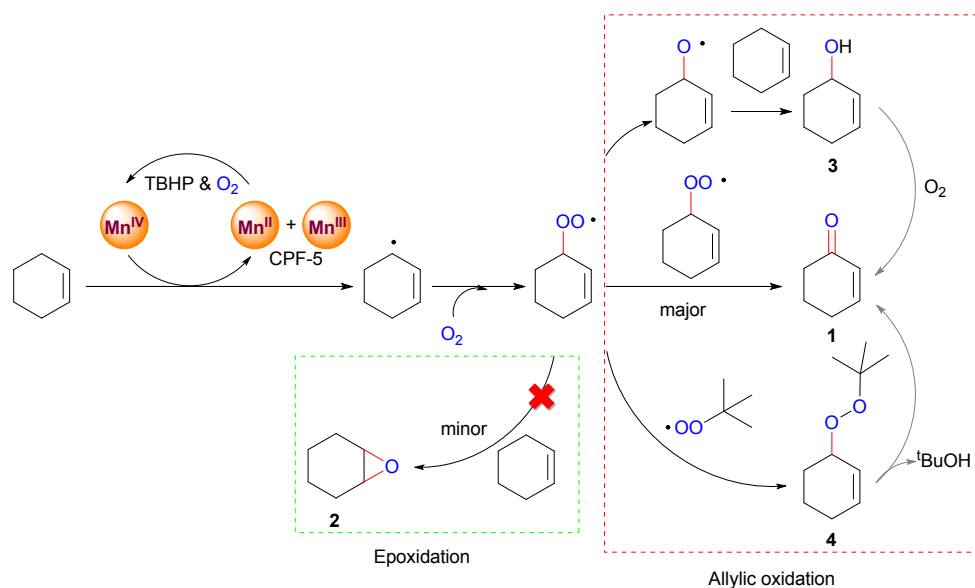


Figure 4. The XPS spectra of (a) CPF-5 and (b) reused CPF-5. The fitted Mn $2p_{3/2}$ peaks for (c) CPF-5 and (d) reused CPF-5. The fitted N 1s peaks for (e) CPF-5 and (f) reused CPF-5.

3.4 Mechanism for the oxidation reaction catalyzed by CPF-5

Based on the experimental results, a plausible reaction mechanism of the CPF-5 catalyzed

oxidation of cyclohexene is proposed (Scheme 1). 3-Cyclohexenyl radical generates at a Mn^{IV} site^{62,63} of CPF-5 and reacts with O_2 to generate a peroxy radical. Then, the peroxy radical reacts to give the cyclohexenone product. Another two reaction pathways in the box surrounded by the red dash lines could lead to the other two allylic oxidation products (**3** and **4**), which could be further oxidized or transformed to cyclohexenone. On the other hand, the reaction between peroxy radical and cyclohexene is not favored, preventing the formation of the epoxide product **2**.



Scheme 1. Proposed reaction mechanism of the CPF-5 catalyzed oxidation of cyclohexene.

4. Conclusion

In conclusion, a redox manganese MOF was synthesized and applied in the selective oxidation of cyclohexene to α,β -unsaturated ketone under mild reaction conditions. Atmospheric oxygen was used instead of stoichiometric chemical oxidants, 87% of selectivity toward cyclohexenone

was achieved with 0.25 equiv. of TBHP as an additive. On the contrary, using a large excess amount of TBHP decreased the product selectivity. More Mn^{IV} species were detected by XPS analysis after the oxidation reaction, which could serve as the catalytic active species. CPF-5 shows higher catalytic activity in selective oxidation of cyclohexene than that of manganese salt, which may originate from the change of coordination environment of Mn in CPF-5. CPF-5 could be reused at least five times with stable activity and slightly decreased selectivity, which could be related to the partial degradation of the framework.

Acknowledgements

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Electronic supplementary material: a detailed synthetic procedure of catalyst, characterization of the ligand and CPF-5 crystal, other catalytic results.

Notes and References

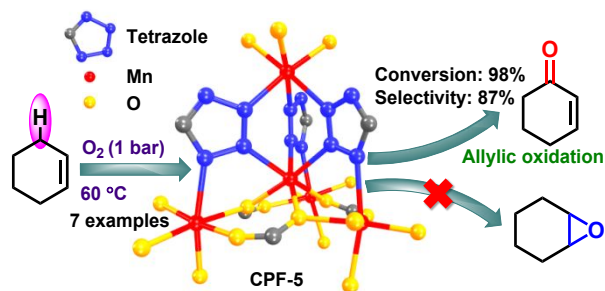
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TOC



Manganese-based CPF-5 as highly efficient catalyst for the selective aerobic oxidation of cyclohexene to cyclohexenone under mild conditions.