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Article

Optimization of Reaction Conditions for Cyclohexane to Cyclohexanone with *t*-Butylhydroperoxide Over $CuCl_2$ Loaded with Activated Carbon

Xiaoling Sun,* Xinhui Zhang, Xiaoyan Cao and Xiaoyan Zhao

*School of Chemical and Environmental Engineering, Shanghai Institute of Technology,
201418 Shanghai, China*

Catalytic oxidation of hydrocarbons can be performed efficiently in the presence of *tert*-butylhydroperoxide (TBHP) under a low-valent transition metal as the catalyst. $CuCl_2$ loaded with activated carbon had synthesized and characterized by X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX), and then utilized as a catalyst for the oxidation of cyclohexane with molecular oxygen as the oxidant and the TBHP as the pro-oxidant under various conditions. The possible reaction mechanism was discussed and the effects of different factors on the oxidation of cyclohexane were investigated. Reaction conditions including catalyst type, oxidant, reaction time, reaction temperature, TBHP amount, solvent type and solvent amount were systematically optimized in order to achieve the highest conversion of cyclohexane and highest selectivity of cyclohexanone. Various other alkanes exhibited higher catalytic activity under the optimal conditions.

Keywords: cyclohexane, cyclohexanone, cyclohexanol, oxidation, $CuCl_2$

Introduction

Labinger and Bercaw[1] pointed out that the selective oxidation of hydrocarbons involving the activation of C–C or C–H bonds is challenging in modern chemistry. Transition metal complexes have attracted attention as reaction catalysts in C–H bond activation under mild conditions.[2] The complexes of porphyrin and phthalocyanine are the most common catalyst in the oxidation of cyclohexane. *L*-Cysteine as the cocatalyst on the oxidation of cyclohexane by *tert*-butylhydroperoxide (TBHP) catalyzed by manganese tetraphenylporphyrin could significantly increase the selectivity of cyclohexanol, which the conversion rate of cyclohexane is 29.8% and ratio of ketone/alcohol is 0.43%.[3] Xie and Zhang[4] explored three types of unsupported and boehmite supported *trans*-A_2B_2-metalloporphyrin chloride complexes. The boehmite supported metalloporphyrins Co-D(p-Cl)PPCl/BM (boehmite or böhmite is an aluminium oxide hydroxide (γ-AlO(OH)) mineral, a component of the aluminium ore bauxite) has high catalytic activity in cyclohexane oxidation under dioxygen that the cyclohexane conversion and selectivity to KA oil (a mixture of cyclohexanone and cyclohexanol) are 6.83 and 83.30%, respectively. .[4] In a temperature range of 300-400 °C at 1 atm of air, the conversion percent of cyclohexane is 32.6% with 37.3% selectivity of cyclohexanol and cyclohexanone, catalyzed by 10% cobalt phthalocyanines supported on γ-alumina.[5] It has been demonstrated that two kinds of catalysts have low selectivity, and the phthalocyanines catalysts need high reaction temperature.

When using molecular oxygen as oxidant in a solvent-free system, 9.87% conversion of cyclohexane were achieved over Au@TiO_2/MCM-41 (Mobil Composition of Matter No. 41) catalysts at 423 K for 2.5 h.[6] $[AuCl_2(\eta^2\text{-Tpm}^{OH})]Cl$ was used for the oxidation of cyclohexane to cyclohexanol and cyclohexanone [Tpm = $HC(pyrazol\text{-}1\text{-}yl)_3$], yields up to 16 and 10% under heterogeneous and homogeneous mild conditions with aqueous H_2O_2, respectively.[7] Two types of gold complex are too costly to mitigate for the benefits it provides. $[Cu_4(L_1)_2(\mu_4\text{-O})(\mu_2\text{-}CH_3COO)_2(\mu_{1,1}\text{-}N_3)(N_3)]$ has the maximum catalytic activity with 47.5% conversion of cyclohexane to cyclohexanol (29.3%) and cyclohexanone (18.2%) when $n(H_2O_2)/n(\text{catalyst})$ ratio is 200 with the reaction time 48 h at room temperature [HL_1 = 2,6-bis(morpholinomethyl)-4-*tert*-butylphenol].[8] Li and Wu[9] found a nearly 100% selectivity rate for cyclohexanone and a 24.4% conversion rate for cyclohexane with the phenanthroline-$CuCl_2$ complex. However, the reaction time lasted for 72 h. Tsunoji and Ide[10] succeeded

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*e-mail: xiaolingsun1@msn.com

in the immobilization of Ti^{IV} acetylacetonate onto the interlayer surfaces of a layered silicate Hiroshima University Silicate-2, $Si_{20}O_{40}(OH)_4 \cdot 4[C_5H_{14}NO]$ (HUS-2), and the Ti-incorporated HUS-2 showed a high photocatalytic activity and excellent chemoselectivity in the cyclohexane oxidation under simulated solar light irradiation. Hassan and Sohaila[11] showed that the nonsymmetrical Schiff base Cu^{II}(saldien)$(H_2O)]^+$ has high activity and selectivity toward cyclohexane oxidation (i.e., cyclohexanol 37% and cyclohexanone 54%) with H_2O_2 as the terminal oxidant. Anisia and Kumar[12] found that the conversion rate of cyclohexane is 14.2% and the selectivity of cyclohexanone is 87.4% at 190 °C when the bimetallic macrocyclic Fe-Cu complex is used as a catalyst to oxidize cyclohexane with molecular oxygen.[13] Various types of Ti-containing zeolites, i.e., Ti-MWW zeolite, have been displayed the highest selectivity and yield for cyclohexanone and cyclohexanol with values of 90.1 and 9.64% for the liquid-phase oxidation of cyclohexane using *t*-butyl hydroperoxide (TBHP, 7-8 wt.%) as model oxidant at 80 °C, respectively.[14] The V-MCM-41 samples were effective in the oxidation of cyclohexane, and the conversion of cyclohexane increased with the vanadium content increase, and catalyst the conversion was up to 22.57% when the content of V-MCM-41 was over 8.1%.[13] These catalysts are difficult to obtain and to be applied to production in the industry. In addition, researchers investigated other catalysts, among which Cu-based catalysts showed high cyclohexanone selectivity and high cyclohexane conversion rates.[15-20]

Oxidizing organic compounds with an environmental-friendly oxidant remains a challenging task in catalytic chemistry. In this context, we have synthesized $CuCl_2$ loaded with activated carbon based on the previous method and applied it as a catalyst to catalytic oxidation of cyclohexane. The $CuCl_2$/AC is fine chemical products with high-value-added and broad prospects, which possess advantages of wide raw material sources, simple synthesis method and low cost. In addition, the catalyst featured higher yield and better product quality within a short period under mild conditions. It could be reused many times without polluting the environment. The effects of different experimental parameters, including catalyst type, oxidant type, reaction time, temperature, TBHP amount, solvent type and solvent amount were further investigated to optimize reaction conditions.

Experimental

Catalyst preparation

A small amount of granular $CuCl_2.2H_2O$ was placed into a watch glass. The sample was dried in vacuum at 120 °C for 6 h to obtain anhydrous $CuCl_2$. Dried AC was then added (3.0 g, 0.25 mol) after dissolving $CuCl_2$ (1.0 g, 5.8 mmol) in anhydrous ethanol (10.0g). The solution was mixed and then passed through N_2 at 150 °C for 12 h until aqueous evaporation. The resulting catalyst was then analyzed at room temperature.

Catalytic activity measurement

In a 100 mL three-necked flask placed in a temperature controlled chamber, the reaction catalyst was added to a cyclohexane solution in acetonitrile. While there is no organic solvent added, the catalytic activity would be decreased. The mixture was stirred with a magnetic stirrer at 500 rpm for 30 min. The reaction was then initiated by adding TBHP in the presence of oxygen. The reaction started post-treatment after a certain period.

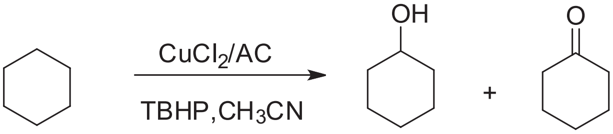

Figure 1. Oxidation of cyclohexone catalyzed by $CuCl_2$/AC.

The post-processing method was as follows. In brief, the reacting solution was cooled to room temperature and then added with 25 mL of 25% sulfuric acid. The solution was extracted twice with anhydrous ether and then twice with saturated aqueous $NaHCO_3$. The extract was then dried using anhydrous $MgSO_4$. The reaction mixture was concentrated on a rotary evaporator under reduced pressure. After adding an internal standard, chlorophenyl, the reaction mixture was examined through gas chromatography.

Results and Discussion

Characterization of catalyst

In our research group, we have synthesized and characterized $CuCl_2$ loaded with activated carbon. The X-ray diffraction (XRD) patterns were recorded on a Panalytical PW 3040/60 X'Pert PRO diffractometer with Cu Kα radiation. The diffraction patterns at 40 kV and 40 mA were recorded within the 5° to 80° Bragg angle (2θ) range at a rate of 5° min^{-1}. Two activated carbon peaks were detected at 2θ = 26.6° and 54.7° (Figure 2). This peak pattern is in accordance with the XRD spectra of fresh activated carbon. A number of peaks for $CuCl_2$/AC were detected at 2θ = 16.2°, 21.9°, 28.88°, and 33.9°, thereby confirming its successful preparation.[21] Besides, the microstructure and constitution of $CuCl_2$/AC were studied with energy-dispersive X-ray spectroscopy

(EDX) analysis techniques. EDX S3400 scanning electron microscope was used to copper chloride component detection and analysis. Figure 3 is an EDX spectrum of supported copper chloride. Table 1 has the corresponding element mass ratio and the atomic ratio values of supported copper chloride. The atomic ratio of Cl content to Cu content was 1.95:1, which is closer to 2:1. These data prove that $CuCl_2$ had been supported on activated carbon.

Table1. Atomic and mass ratio of supported copper chloride

Element	wt.%	at.%
C	23.77	30.21
O	66.45	66.32
Cl	5.10	2.30
Cu	4.68	1.18

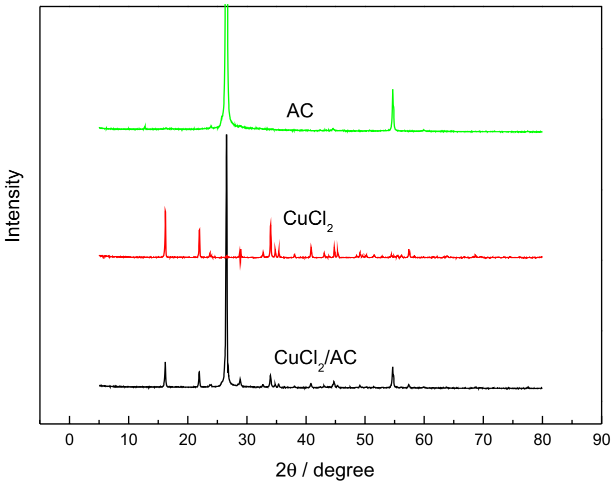

Figure 2. XRD of AC, $CuCl_2$ and $CuCl_2$/AC.

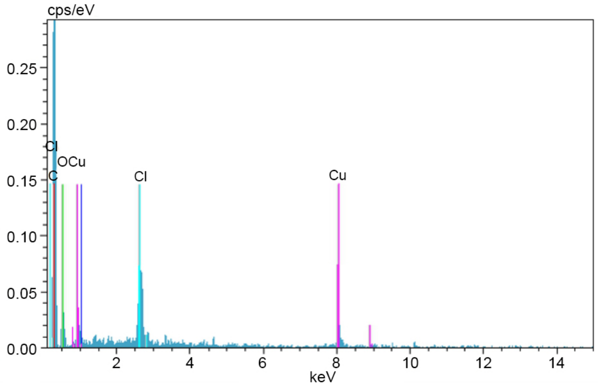

Figure 3. Energy dispersive X-ray spectrum of supported $CuCl_2$.

Catalytic activity effect of catalyst type on cyclohexane oxidation

It is interesting to observe that, by the addition of $CuCl_2$ and $CuCl_2$/AC as a catalyst for comparison, two kinds of catalysts have considerable activity (Table 2). The conversion rate of cyclohexane was 33.73% when $CuCl_2$ was used as catalyst. The reaction have weakness, one is responding to low selectivity, one is producing more by-product. While, when using $CuCl_2$/AC as a catalyst, the selectivity of cyclohexanone and cyclohexanol was as high as 87.99%. Check experiments show that no cyclohexanol or cyclohexanone are formed in the absence of the catalysts under the same conditions. As well, the oxidation reaction of cyclohexane does not happen only using activated carbon as catalyst.

Effect of oxidant on cyclohexane oxidation

Table 3 shows the influence of oxidants on cyclohexane conversion. Only a small portion of cyclohexane was oxidized because the reaction system did not contain TBHP. Cyclohexanone selectivity decreased after adding TBHP, although the conversion rates were relatively high without oxygen feeding. The maximum cyclohexane conversion and cyclohexanone selectivity rates were obtained when TBHP and molecular oxygen were used as co-oxidants. This result implies that using molecular oxygen as the oxidant and TBHP as the pro-oxidant significantly improves the catalytic efficiency of cyclohexanone.

Effect of reaction time on cyclohexane oxidation

Table 4 shows the influence of reaction time on cyclohexane oxidation. Cyclohexanol yield and selectivity changed regardless of time, but cyclohexanone yield peaked at 2 h reaction time and declined as the reaction proceeded. This result can be attributed to the fact that the functional groups of cyclohexanone and cyclohexanol are more active than that of cyclohexane and are easily oxidized to adipic acid, glutaric acid, and other small molecules in

Table 2. The influence of catalyst type to the cyclohexane conversion

Catalyst type	Cyclohexanone		Cyclohexanol	
	Yield / %	Selectivity / %	Yield / %	Selectivity / %
$CuCl_2$	13.39	39.69	10.36	30.71
$CuCl_2$/AC	7.18	68.38	2.06	19.61

Fixed reaction conditions: 5.0 g cyclohexane, 10.0 mL acetonitrile, 0.2 g catalyst, 3.0 mL TBHP, 30 mL min^{-1} O_2, 8 h, 50 °C.

Table 3. The influence of oxidant to the cyclohexane conversion

Oxidant	time / h					
	0.5	1.0	1.5	2.0	3.0	4.0
O_2	0.17	0.25	0.75	0.92	1.04	1.08
TBHP	10.77	12.34	12.65	13.76	15.73	16.12
TBHP/O_2	11.13	12.36	13.41	14.08	16.67	17.56

TBHP: *tert*-butylhydroperoxide. Fixed reaction conditions: 5.0 g cyclohexane, 10.0 mL acetonitrile, 0.2 g $CuCl_2$/AC, 3.0 mL TBHP, 30 mL min^{-1} O_2, 50 °C.

the catalytic process. Moreover, the functional group of cyclohexanone is more stable than that of cyclohexanol. These results imply that 2 h is the optimum reaction time to obtain the maximum yield of cyclohexanone. At this point, the conversion rate of cyclohexane was 16.27%.

Effect of reaction temperature on cyclohexane oxidation

The effect of reaction temperature was initially studied under a temperature range of 25-90 °C (Table 5). The selectivity and yield of cyclohexone increased with temperature, peaked at 70 °C, and then declined. The effect of the reaction temperature was mainly determined by three conditions. First, a radical reaction at high temperatures increased free radical generation. Second, extremely high temperatures reduced the amount of dissolved oxygen in the solvent and hence decreased the amount of raw materials in the reaction. Third, cyclohexane easily vaporized with increasing temperature and had insufficient time to participate in the reaction. Therefore, the optimum condition for the reaction temperature was 70 °C, and the conversion rate of cyclohexane was 17.33%.

Effect of TBHP amount on cyclohexane oxidation

TBHP is a radical reaction initiator. Using a small amount of TBHP in the reaction corresponded to low free oxygen content. Large amounts of TBHP can reduce the cyclohexanone yield because the product can be oxidized by the initiator to form by-products, such as small molecule acids. As shown in Table 6, 5 mL of TBHP was determined as the optimal amount for cyclohexane oxidation. The conversion rate of cyclohexane was 19.45%.

Effect of solvent type on cyclohexane oxidation

The results of effect of solvent type are listed in Table 7. Table 7 shows that, the oxidation reaction have higher yield and catalytic selectivity when using polar aprotic solvent. Among polar aprotic solvents, the optimum solvent for the reaction is acetonitrile. As shown in Table 7, differences exist among the cyclohexane oxidation because of their various solvents. Thus, the key

Table 4. Influence of the reaction time to the oxidation of cyclohexane

time / h	Cyclohexanone		Cyclohexanol	
	Yield / %	Selectivity / %	Yield / %	Selectivity / %
0.5	5.95	55.14	3.00	27.49
1.0	7.29	58.27	2.71	20.65
2.0	9.38	58.79	3.33	21.50
3.0	8.20	59.33	2.78	20.57
3.5	8.30	60.66	2.94	21.08
4.0	7.71	60.68	2.48	19.63

Fixed reaction conditions: 5.0 g cyclohexane, 10.0 mL acetonitrile, 0.2 g $CuCl_2$/AC, 3.0 mL TBHP, 30 mL min^{-1} O_2, 50 °C.

Table 5. Influence of the reaction temperature to the oxidation of cyclohexane

Temperature / °C	Cyclohexanone		Cyclohexanol	
	Yield / %	Selectivity / %	Yield / %	Selectivity / %
25	5.17	56.28	2.18	23.29
40	6.63	60.67	2.71	22.16
50	9.70	63.86	3.60	18.67
70	11.30	70.99	3.39	18.17
90	11.16	67.64	3.07	16.54

Fixed reaction conditions: 5.0 g cyclohexane, 10.0 mL acetonitrile, 0.2 g $CuCl_2$/AC, 3.0 mL TBHP, 30 mL min^{-1} O_2, 2 h.

Table 6. Influence of the amount of TBHP to the oxidation of cyclohexane

Amount of TBHP / mL	Cyclohexanone		Cyclohexanol	
	Yield / %	Selectivity / %	Yield / %	Selectivity / %
1.0	1.01	26.35	0.59	1.25
2.0	2.59	45.68	0.85	1.43
3.0	3.83	51.82	1.17	15.01
4.0	7.34	54.14	3.30	24.13
5.0	13.02	67.51	3.72	20.91
6.0	8.25	66.20	2.83	19.39
7.0	7.00	60.43	2.07	19.57

Fixed reaction conditions: 5.0 g cyclohexane, 10.0 mL acetonitrile, 0.2 g $CuCl_2$/AC, 30 mL min^{-1} O_2, 2 h, 70 °C.

Table 7. Influence of the type of solvent to the oxidation of cyclohexane

Type of solvent / mL	Cyclohexanone		Cyclohexanol	
	Yield / %	Selectivity / %	Yield / %	Selectivity / %
Ethanol	7.47	59.47	3.50	27.86
Acetic acid	7.30	57.25	4.40	34.50
Ethyl acetate	6.50	53.49	4.69	38.60
Dimethylsulfoxide	11.44	68.05	3.50	20.82
Acetonitrile	13.02	67.51	3.72	20.91
n-Hexane	7.65	54.17	6.51	43.55
1,2-Dichloroethane	6.74	57.95	4.65	39.98

Fixed reaction conditions: 5.0 g reaction material, 10.0 mL solvent, 0.2 g $CuCl_2$/AC, 5.0 mL TBHP, 30 mL min^{-1} O_2, 2 h, 70 °C.

to the high yield and catalytic selectivity of cyclohexanone lies in selecting appropriate solvents.

Effect of solvent amount on cyclohexane oxidation

The amount of solvent was another parameter that influenced the yield of cyclohexane oxidation and thus should be further optimized. The results are listed in Table 8. Table 8 illustrates that the selectivity and yield of cyclohexane oxide are in relation to the amount of acetonitrile. The selectivity of cyclohexanone easily reached to 67.51% when the amount of acetonitrile was equal to 10 mL. However, the selectivity of cyclohexanol changed irregularly with acetonitrile increasing because of its instability. Therefore, the amount of acetonitrile of 10 mL was selected as the optimal amount for the oxidation of cyclohexane.

Catalytic activity of other alkanes

Copper chloride had the strongest effect on the oxidation of alkane. The catalytic activities of other alkanes are listed in Table 9; allylic exhibited the highest catalytic activity among the tested alkanes. As shown in Table 9, α-pinene and 3-carene exhibited conversion rates as high as 100% and had high selectivity for ketone. It is a promising

Table 8. Influence of the amount of solvent to the oxidation of cyclohexane

Amount of solvent / mL	Cyclohexanone		Cyclohexanol	
	Yield / %	Selectivity / %	Yield / %	Selectivity / %
0	7.50	56.68	4.45	33.71
5.0	8.41	62.76	2.85	21.27
10.0	13.02	67.51	3.72	20.91
15.0	8.90	64.72	3.21	23.34
20.0	7.80	53.79	1.80	12.41

Fixed reaction conditions: 5.0 g cyclohexane, 0.2 g $CuCl_2$/AC, 5.0 mL TBHP, 30 mL min^{-1} O_2, 2 h, 70 °C.

Table 9. Catalytic oxidation on the other substrates

Compound	Conversion / %	Product/Yield / %
Methylbenzene	62.3	benzaldehyde 28.16, phenylcarbinol 33.90
Diphenylmethane	84.7	benzophenone 84.70
α-Pinene	100.0	verbenone 75.40
3-Carene	100.0	3-carene-2,5-diketone 61.20

Fixed reaction conditions: 5.0 g reaction material, 10.0 mL acetonitrile, 0.2 g $CuCl_2$/AC, 5.0 mL TBHP, 30 mL min^{-1} O_2, 2 h, 70 °C.

Table 10. Recyclability of $CuCl_2$/AC

Usage count	Cyclohexane conversion / %	Cyclohexanone		Cyclohexanol	
		Yield / %	Selectivity / %	Yield / %	Selectivity / %
1	19.45	13.02	66.94	3.72	19.13
2	19.27	12.91	67.00	3.64	18.89
3	19.25	12.87	66.86	3.61	18.75
4	18.55	11.30	60.92	3.14	16.93
5	18.01	10.12	56.19	2.93	16.27

Fixed reaction conditions: 5.0 g cyclohexane, 10.0 mL acetonitrile, 0.2 g $CuCl_2$/AC, 5.0 mL TBHP, 30 mL min^{-1} O_2, 2 h, 70 °C.

catalyst with a high catalytic activity for cyclohexone oxidation under optimal reaction conditions. However, the recyclability of this catalyst needs further investigation.

Recyclability of the catalyst

Table 10 shows the selection of optimum conditions to study catalyst life in the reaction. The $CuCl_2$ catalyst can be reused five times without losing its catalytic activity. Therefore, using this catalyst can decrease production cost, improve reaction yield, and reduce environmental pollution in oxidation reactions. Hence, we selected $CuCl_2$ as a catalyst for cyclohexane oxidation.

Mechanistic studies

On the basis of the experimental results, the oxidation of cyclohexane to cyclohexanone with molecular

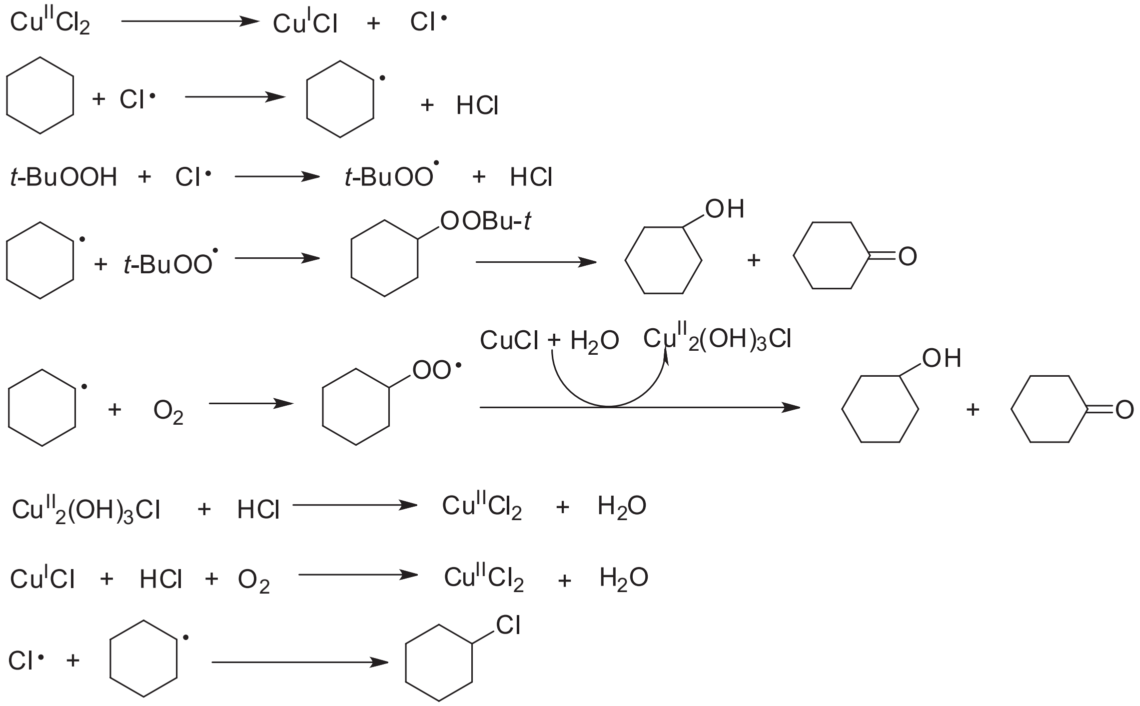

Figure 4. Reaction mechanism for the oxidation of cyclohexane catalyzed by $CuCl_2$/AC.

oxygen under the catalysis of $CuCl_2$/AC was considered a radical reaction. Both molecular oxygen and TBHP were involved in the oxidation reaction. On the one hand, the transition intermediate of molecular oxygen was cyclohexylhydroperoxide, which was oxidized to cyclohexanol and cyclohexanone under the catalysis of $CuCl_2$. On the other hand, TBHP produced cyclohexyl peroxide *tert*-butyl, which consequently generated cyclohexanol and cyclohexanone. The mechanisms of molecular oxygen and TBHP were similar, but experimental data reflected that the oxidation efficiency of TBHP was significantly higher than that of molecular oxygen. Cyclohexanone selectivity was slightly improved when molecular oxygen was used as the oxidant and TBHP was used as the pro-oxidant. Moreover, cyclohexanone was easily produced in the presence of molecular oxygen. The electronic configuration of the transition metal $CuCl_2$ contained variable valence metal ions by alternately being involved in the reaction. As a result, it increased the free radical contents of the reactants and intermediates. A large amount of chlorocyclohexane was generated after the addition of $CuCl_2$ and $FeCl_3$. This result validates the mechanisms of cyclohexane. New methods for generating chlorocyclohexane must be explored in future studies.

Conclusions

The reaction conditions for the oxidation of cyclohexane were optimized. Maximum cyclohexone conversion (19.45%) and cyclohexanone selectivity (67.45%) rates were achieved when the reaction time, reaction temperature, and TBHP amount were 2 h, 70 °C and 5 mL, respectively.

Acknowledgements

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