



Metal chlorides-catalyzed selective oxidation of cyclohexane by molecular oxygen under visible light irradiation

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ABSTRACT

The development of mild and efficient process for the selective oxidation of organic compounds with molecular oxygen can be one of the key technologies for synthesizing oxygenates. Here, a visible light-driven metal chloride to catalyze the selective oxidation of cyclohexane was carried out at ambient temperature under a pure O₂ atmosphere. Among the metal salts examined, only a few metal chlorides, with easily changeable valence, such as CuCl₂·2H₂O, VOCl₃, and FeCl₃·6H₂O, were found to be active to this photo-oxidation reaction in acetonitrile or acetone, providing cyclohexanol, cyclohexanone, chlorocyclohexane, and cyclohexene as main products. This is likely because the weak coordination of these metal chlorides with solvent molecules plays key roles in absorbing visible light and realizing photoredox cycle, as supported by UV–Vis spectrum and cyclic voltammetry measurements. Among these active metal chlorides, CuCl₂·2H₂O showed a higher conversion and better selectivity for cyclohexanol and cyclohexanone (the oxygenated products) than the other two metal chlorides, and its activity and selectivity for chlorocyclohexane were significantly improved in the case of adding concentrated HCl, because HCl promotes the photocatalytic cycling, as supported by UV–Vis spectra. Notably, a high turnover frequency (TOF, 7.4 h⁻¹) and an excellent selectivity for the oxygenated products (93%) were achieved upon a low concentration of CuCl₂·2H₂O (0.002 mol L⁻¹), 0.1 ml of concentrated HCl and 2 atm of O₂ pressure. Based on these findings, a free radical mechanism for the present photocatalysis system was proposed.

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1. Introduction

Oxidation of cyclohexane by molecular oxygen continues to be a very important and challenging process [1], because cyclohexanone, one of the main products of this reaction, is a key intermediate in the production of nylons [2] and the synthesis of a variety of fine chemicals [3]. In industrial process, large-scale oxidation of cyclohexane to cyclohexanol and cyclohexanone is carried out with air using cobalt salt catalysts under relatively harsh conditions (temperatures of 443–503 K and pressures of 10–15 bar) [4], and cyclohexane conversion in this process is limited to lower than 10% in order to obtain a relatively high selectivity for the goal products (ca. 70%) [5–7].

Various new catalytic routes have been explored for selective oxidation of cyclohexane to cyclohexanol and cyclohexanone by dioxygen or air [2,8]. However, most of these methods require stoichiometric reducing agent or photosensitization with a UV

source [9–11], which may constitute serious economical impediments for large-scale applications. To overcome these obstacles, some catalytic processes with Cr- [12] or Co-substituted [13] AlPO-5 zeolite, NHPI-Co(acac)_n [14,15], Fe-porphyrin [16–18], and Cu-phenanthroline complex/K₂CO₃ [19] as catalysts have been developed to efficiently accelerate this reaction in the absence of reducing agents.

Photocatalytic oxidation has received enormous attention during recent years, because of its potential application in environmental treatment and the synthesis of fine chemicals [20,21]. On the other hand, the use of solar light and molecular oxygen as reagents in oxidative catalysis contributes to realizing innovative and economically advantageous processes for conversion of hydrocarbons into oxygenates and, at the same time, to move toward a sustainable chemistry that has a minimal environmental impact. Up to now, some progresses have been made in the field of UV or visible light-driven aerobic oxidation of cyclohexane catalyzed by TiO₂ [22–26], Fe–TiO₂ [27], Cr–SiO₂ [28], V₂O₅–Al₂O₃ [29], NaY zeolite [30–32], trans-dioxoosmium(vi) complex [33], or Fe (III)

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porphyrin complexes [34,35]. In particular, iron(III) chloride [36–38] and copper(II) chloride [39] are able to promote aerobic oxidation of cyclohexane under light irradiation with $\lambda > 300$ nm, yielding cyclohexanol and cyclohexanone as major products. However, photocatalytic activity of the metal salts reported up to now is still unsatisfying, and how to mediate their photocatalytic performance is hardly concerned, and the correlative photocatalytic mechanism is still ambiguous. Herein, we report initial results obtained upon using the visible light-driven various metal salts to catalyze aerobic oxidation of cyclohexane in different solvents.

2. Experimental

2.1. Materials and apparatus

Materials and reagents used in this study were cyclohexane, *n*-hexanol, acetonitrile (CH₃CN), acetone (CH₃COCH₃), ethyl acetate, copper(II) chloride (CuCl₂·2H₂O), iron chloride (FeCl₃·6H₂O), cuprous chloride (CuCl), copper(II) bromide (CuBr₂), copper(II) nitrate (Cu(NO₃)₂·3H₂O), copper(II) acetate (CuAc₂), and other metal chlorides, all of which were of analytical grade. Distilled water was used throughout this experiment.

2.1.1. UV-Vis spectrophotometer

The liquid UV-Vis spectra of samples were recorded from 200 to 800 nm on UV-2450 spectrophotometer (Shimadzu, Japan).

2.1.2. Cyclic voltammetric characterizations of metal salts

In cyclic voltammetric experiments, three-electrode configuration and an autolab electrochemical workstation (Eco Chemie, Holland) were used. The working electrode (WE) was a glassy carbon electrode (GCE, 3-mm diameter disk), the counter electrode was a sheet of platinum foil, and the reference electrode was a KCl-saturated calomel electrode (SCE). All potentials here are reported vs the SCE. All the electrochemical experiments were carried out at room temperature (20 °C).

2.1.3. Procedure of photocatalytic oxidation

Photo-oxidation of cyclohexane was performed in a self-assembled photo-reactor equipped with a water-cooled condenser (15 °C, see Fig. 1), and a 35 W tungsten-bromine lamp with an UV light filter (Osram brand, see Fig. S1 in supporting information) was immersed in the acetonitrile or acetone (5 ml) solution containing cyclohexane (5 mmol) and metal salt catalyst (0.4 mmol). The reaction mixture was stirred magnetically under pure dioxygen atmosphere (1 atm) and sustained visible light irradiation, and the temperature of reaction solution increased to 36–38 °C because of the heating effect of light irradiation (the corresponding temperature profile was given in Fig. S2 of supporting information). After the desired irradiation time had elapsed, a small portion of reaction mixture (0.5 ml) was sampled from the reactor, and the products were quantitatively analyzed on an Agilent 6890N gas chromatograph (GC) with a DB-17 polysiloxane capillary column (30 m × 0.32 mm × 0.50 μm) and flame ionization detector (FID) using *n*-hexanol as an internal standard. Both the injector and detector temperature were 250 °C, and the column temperature was 80 °C. The isolated products were satisfactorily identified by comparing the MS spectra with those of the authentic samples. In addition, with triphenylphosphine to treat the filtrate for 1 h hardly changed selectivity of the products cyclohexanol and cyclohexanone, which showed the absence of alkyl hydroperoxide in the products [40].

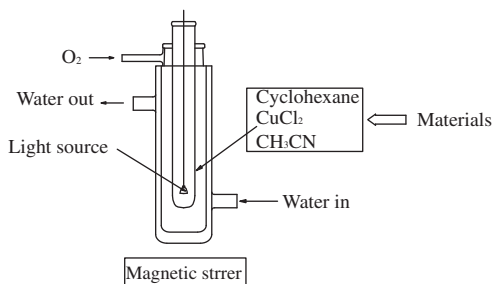


Fig. 1. Self-assembly photo-reactor used in this study.

graph (GC) with a DB-17 polysiloxane capillary column (30 m × 0.32 mm × 0.50 μm) and flame ionization detector (FID) using *n*-hexanol as an internal standard. Both the injector and detector temperature were 250 °C, and the column temperature was 80 °C. The isolated products were satisfactorily identified by comparing the MS spectra with those of the authentic samples. In addition, with triphenylphosphine to treat the filtrate for 1 h hardly changed selectivity of the products cyclohexanol and cyclohexanone, which showed the absence of alkyl hydroperoxide in the products [40].

3. Results and discussion

3.1. Characterization results

UV-Vis spectra of CuCl₂·2H₂O, CuBr₂, Cu(NO₃)₂·3H₂O, CuCl and FeCl₃·6H₂O in acetonitrile (or other organic solvents), and water are presented in Figs. 2 and 3, respectively. These metal salts generally showed two kinds of characteristic bands: a d-d band assigned to metal ions in a low energy region (500–800 nm) and some charge transfer (CT) bands between metal ions and ligands in high energy region (200–500 nm) [41]; for example, CuCl₂·2H₂O in CH₃CN showed a very weak and broad d-d band near 700–800 nm and three CT bands in 200–470 nm. Among the three CT bands, the first weak CT band at 258 nm, which was observed in all the solvents, is likely assigned to the Cu²⁺O²⁻ → Cu⁺O⁻ transition of Cu²⁺·H₂O [42]. The second strong CT band near 305 nm is likely originated from the Cu²⁺Cl⁻ → Cu⁺Cl transition of CuCl₂ molecules, which was supported by the following facts: A similar CT band was observed in other organic solvents acetone and ethyl acetate (see inset in Fig. 2), but absent in water. The third CT band near 460 nm in MeCN, which a similar band near 473 nm was also observed in acetone (see inset in Fig. 2), is likely assigned to the Cu²⁺Cl⁻ → Cu⁺Cl transition of Cu(MeCN)Cl₂ produced from a weak coordination of CuCl₂ with MeCN molecule [43]. The UV-Vis spectra of aqueous CuCl₂·2H₂O, Cu(NO₃)₂, and CuBr₂ were very similar to each other (see Fig. 3), consisting of one to two CT bands in the 230–400 nm region. The strong CT band near 230 nm was likely originated from the Cu²⁺O²⁻ → Cu⁺O⁻ transition of Cu(H₂O)₆²⁺ ions. The spectral change of CuCl₂·2H₂O in these solvents may be explained with molecular orbital theory: H₂O as electron-donating molecule increases the energy gap between the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) through a coordination effect, leading to blue shift of

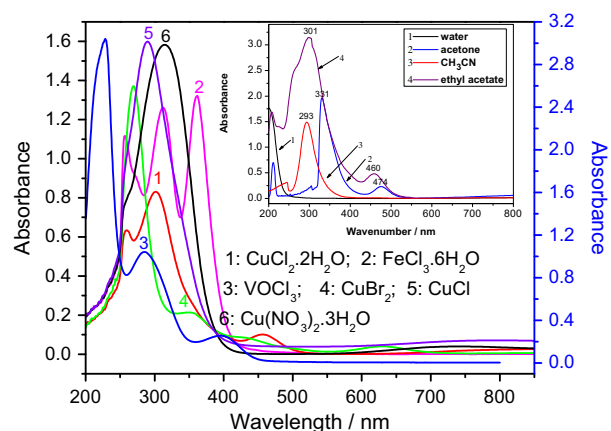


Fig. 2. The UV-Vis spectra of various metal salts in acetonitrile solvent (1.0×10^{-3} mol L⁻¹, 1: CuCl₂·2H₂O; 2: FeCl₃·6H₂O; 3: Cu(NO₃)₂·3H₂O; 4: CuBr₂; 5: CuCl). Inset is the UV-Vis spectra of CuCl₂·2H₂O in various solvents (1.1×10^{-3} mol L⁻¹).

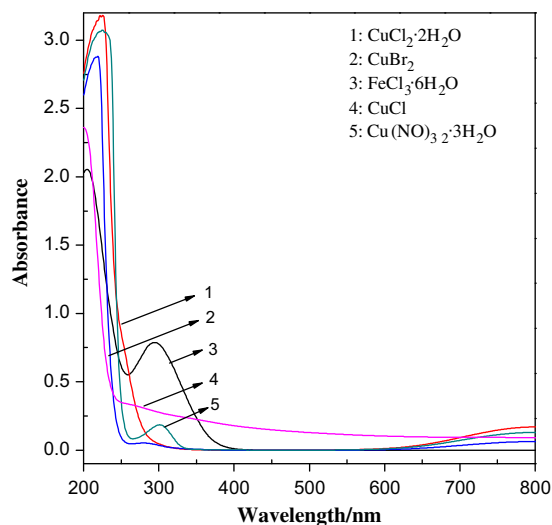


Fig. 3. The UV-Vis spectra of various metal salts in water solvent ($1.0 \times 10^{-3} \text{ mol L}^{-1}$).

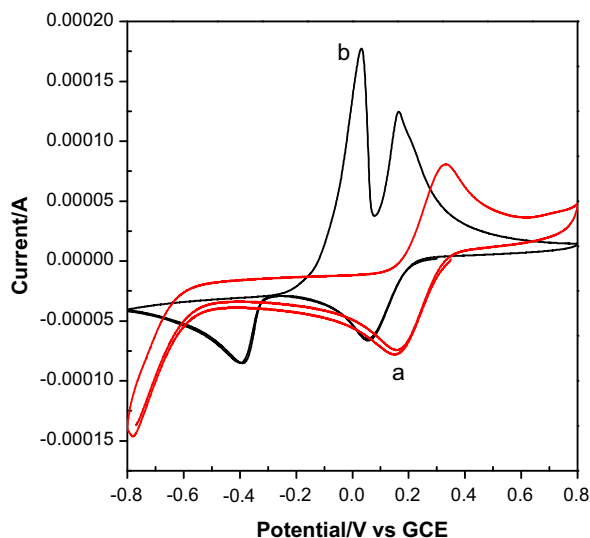


Fig. 4. Cyclic voltammograms of CuCl_2 in acetonitrile ((a) $5 \times 10^{-3} \text{ mol L}^{-1}$) and water ((b) $5 \times 10^{-3} \text{ mol L}^{-1}$). 0.1 mol L^{-1} of tetraethylammonium perchlorate served as the supporting electrolyte.

the CT bands; On the contrary, the coordination effect of acetonitrile or acetone as electron-accepting molecule leads to red shift of the CT bands due to the decrease in HOMO–LUMO energy gap [44]. It was further seen from Figs. 2 and 3 that CuBr_2 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ also absorbed the visible light of 370–550 nm region in CH_3CN , but did not in water. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and CuCl hardly had any response to the visible light of this region whether the solvent used was CH_3CN or water. It is concluded from these findings that the response of metal salts to visible light is dependent on the following factors: (i) the kind and valence state of metal ions, (ii) the kind of anions, and (iii) the kind of solvents. Fig. 4 presents the cyclic voltammograms (CVs) of GCE for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in acetonitrile and water, respectively. Only a pair of quasi-reversible redox waves near $(0.331 + 0.162)/2 = 0.247 \text{ V}$ was observed for 5 mM of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in CH_3CN , being assigned to the redox process between Cu^{2+} and Cu^+ ions. Notably, the $\text{Cu}^{2+}/\text{Cu}^+$ redox waves in the CV of aqueous $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ became shifted to near $(0.162 + 0.057)/2 = 0.110 \text{ V}$. Another pair of irreversible redox peaks was also

observed at $(0.03-0.398)/2 = -0.184 \text{ V}$, which was assigned to the redox process between Cu^+ ions and Cu metals. It is concluded from the CV measurements that the reduction of Cu^{2+} to Cu^+ ions occurs more easily in acetonitrile than water, which is consistent with the UV-Vis spectral results. On the other hand, the further reduction of Cu^+ to Cu^0 in acetonitrile is inhibited in the present scanning potential range, but easily proceeds in water, implying that the redox cycle between Cu^{2+} and Cu^+ ion is realized more easily in acetonitrile than in water.

3.2. Photo-oxidation results

3.2.1. Photocatalytic performance of various metal salts

Table 1 lists data for some metal salts-catalyzed oxidation of cyclohexane with O_2 at 36–38 °C under visible light irradiation. Entries 1–8 illustrate that the metal chlorides with a negative standard redox potential (SRP) showed very poor photocatalytic activity less than 1% conversion in CH_3CN solvent, while a few metal chlorides, such as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and VOCl_3 , with a positive SRP were found to be active to this photo-oxidation reaction, affording cyclohexanol, cyclohexanone, chlorocyclohexane, and cyclohexene as major reaction products (see entries 9, 12, and 13). Among them, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ showed the best photocatalytic activity, providing about 22.1% of cyclohexane conversion with a relatively high selectivity for the oxygenated products (57%) after 8 h of visible light irradiation (see entry 9). And it still exhibited good activity when the reaction solution was irradiated from its outside by visible light (entry 10). However, when the lamp was packaged by silver paper, the catalytic activity of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was nearly neglected, even if the solution temperature went up from 15 to 36–38 °C because of the heating effect of lamp (see entries 11). These findings undoubtedly support that the oxidation reaction is triggered by light irradiation rather than heating effect. In comparison with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ exhibited a higher chlorocyclohexane selectivity (57%, see entry 12) and VOCl_3 gave a considerable amount of cyclohexene (20% selectivity, see entry 13) under the same reaction conditions. Entries 14–17 illustrate that other anion-containing copper compounds, including CuBr_2 to respond to visible light, were nearly inactive to this photo-oxidation.

The influence of solvents on the photocatalytic oxidation was further examined by using the best catalyst $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The photocatalytic reaction hardly occurred in water and ethyl acetate (see entries 18–19), whereas it could proceed efficiently in MeCN and acetone (entries 9 and 20). This corresponded well with the adsorption ability of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to visible light in these solvents, as supported in UV-Vis spectral characterization. Notably, the photocatalysis in acetone medium was more selective to the formation of oxygenated products (68%) than in MeCN one, being probably due to the better solubility of cyclohexane in acetone than MeCN. The present photocatalysis system, being different from the TiO_2 -photocatalyzed cyclohexane oxidation previously reported by some authors [22–26], can provide a small amount of cyclohexene and a higher proportion of cyclohexanol than cyclohexanone in products. From the photo-oxidation results of cyclohexanol and chlorocyclohexane catalyzed by $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ under the present conditions (see entries 21 and 22), we may find answers that the formation of cyclohexene is due to the further transformation of chlorocyclohexane, and a further oxidation of cyclohexanol to cyclohexanone is existent, but $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ shows a relatively low photocatalysis activity for this reaction.

3.2.2. Effect of various parameters

In the following experiments, the influence of the concentration of catalyst $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and substrate cyclohexane, irradiation time, as well as the amount of water on the photo-oxidation, was checked by using acetone or MeCN as a solvent. It was seen from

Table 1
Visible light-driven oxidation of cyclohexane with molecular oxygen catalyzed by various metal salts.^a

Cyclohexane $\xrightarrow[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}]{h\nu, \text{O}_2}$ Cyclohexene + Chlorocyclohexane + Cyclohexanol + Cyclohexanone

Entry	Catalyst	Solvent	Conv. ^b (%)	Selectivity ^c (%)				SRP ^d (V)
				A	B	C	D	
1	ZnCl ₂	MeCN	0	–	–	–	–	E(Zn ²⁺ /Zn) = –0.76
2	AlCl ₃		0.3	73	27	0	0	E(Al ³⁺ /Al) = –1.66
3	CoCl ₂ ·6H ₂ O		0.3	81	19	0	0	E(Co ²⁺ /Co) = –0.28
4	SnCl ₂ ·2H ₂ O		0.6	49	30	14	7	E(Sn ²⁺ /Sn) = –0.14
5	SnCl ₄ ·5H ₂ O		0.2	22	47	27	4	E(Sn ⁴⁺ /Sn ²⁺) = 0.15
6	MnCl ₂ ·4H ₂ O		0.2	33	46	15	6	E(Mn ²⁺ /Mn) = –1.19
7	NiCl ₂ ·6H ₂ O		0.2	31	49	13	7	E(Ni ²⁺ /Ni) = –0.26
8	LaCl ₃ ·xH ₂ O		0.1	45	38	12	5	E(La ³⁺ /La) = –2.38
9	CuCl ₂ ·2H ₂ O		22.1	2	41	43	14	E(Cu ²⁺ /Cu ⁺) = 0.15
10 ^e	CuCl ₂ ·2H ₂ O		17.6	7	46	36	11	
11 ^f	CuCl ₂ ·2H ₂ O		0.5	–	44	33	23	
12 ^g	FeCl ₃ ·6H ₂ O		14.4	2	57	24	17	E(Fe ³⁺ /Fe ²⁺) = 0.77
13 ^g	VOCl ₃		17.2	20	33	29	18	E(VO ³⁺ /VO ²⁺) = 0.99
14	CuAc ₂	MeCN	0	–	–	–	–	E(Cu ²⁺ /Cu ⁺) = 0.15
15	Cu(NO ₃) ₂ ·3H ₂ O		0.2	0	0	58	42	
16	CuBr ₂		0.2	0	0	65	35	
17	CuCl		0.9	37	24	24	15	
18	CuCl ₂ ·2H ₂ O	Water	0	–	–	–	–	E(Cu ²⁺ /Cu ⁺) = 0.15
19		Ethylacetate	0.5	0	0	57	43	
20		Acetone	18.5	2	30	39	29	
21 ^{h,j}		MeCN	4.4	–	–	90.3	5.3	
22 ⁱ			2.1	4.9	91.5	0.7	0.8	

^a Cyclohexane (5 mmol), catalyst (4.0 mmol, 0.08 mol L^{–1}), solvent (5 ml), O₂ (1 atm), temperature (36–38 °C), time (8 h), using 35 W of tungsten–bromine lamp as visible light source.

^b Cyclohexane conversion = (∑ content (mmol) of each product measured via GC analysis/adding cyclohexane amount (mmol)) × 100%.

^c Product selectivity = content of this product/∑ content (mmol) of each product × 100%, A = cyclohexene, B = chlorocyclohexane, C = cyclohexanol, D = cyclohexanone, a trace amount of 1,2-dichlorocyclohexane was also detected by GC–MS method.

^d Standard redox potential in aqueous solution.

^e Two 35 W tungsten–bromine lamps were placed beside reactor.

^f The lamp was packaged by silver paper.

^g Irradiation time, 12 h.

^h Using cyclohexanol (98%) as a substrate.

ⁱ Using chlorocyclohexane (99%) as a substrate.

^j Data listed are the content of various components by GC analysis after photoreaction for 12 h.

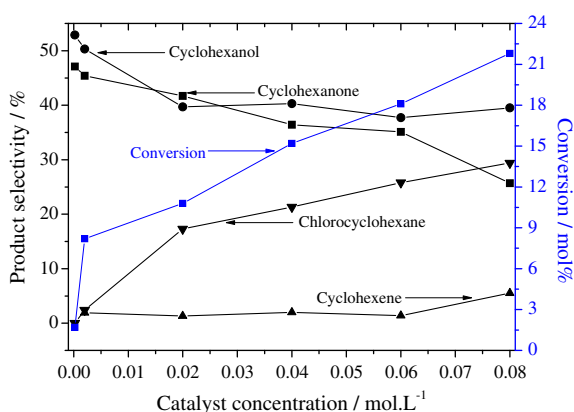


Fig. 5. Effect of CuCl₂·2H₂O concentration on cyclohexane oxidation in acetone (irradiation time, 12 h).

Fig 5 that an increase in the concentration of catalyst from 0.002 to 0.08 mol L^{–1} resulted in continuous and considerable increases of cyclohexane conversion from 10.4% to 21.8% and chlorocyclohexane selectivity from 2% to 29%, respectively, with a concomitant decrease in the selectivity of oxygenated products from 96% to 65%. At the same time, a jade-green Cu₂(OH)₃Cl precipitate that has been identified by X-ray diffraction technique (see Fig. S3 in

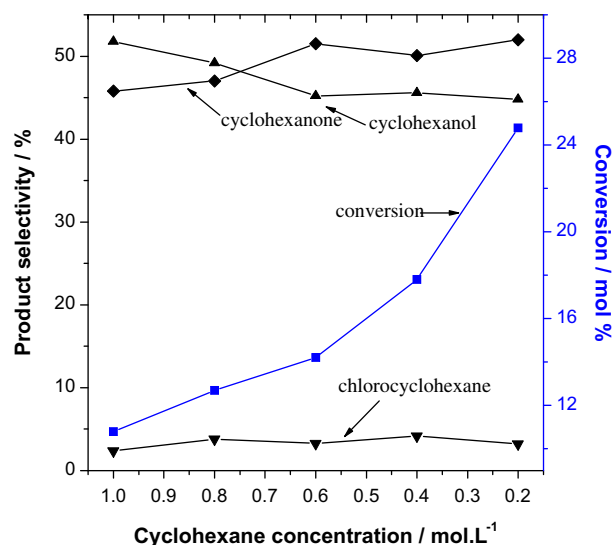


Fig. 6. Effect of cyclohexane concentration on the CuCl₂·2H₂O-photocatalyzed reaction in MeCN (irradiation time, 8 h).

supporting information), was formed upon high catalyst concentration. These findings indicate that the photocatalysis cycling of CuCl₂·2H₂O encounters impediments, because the formation of

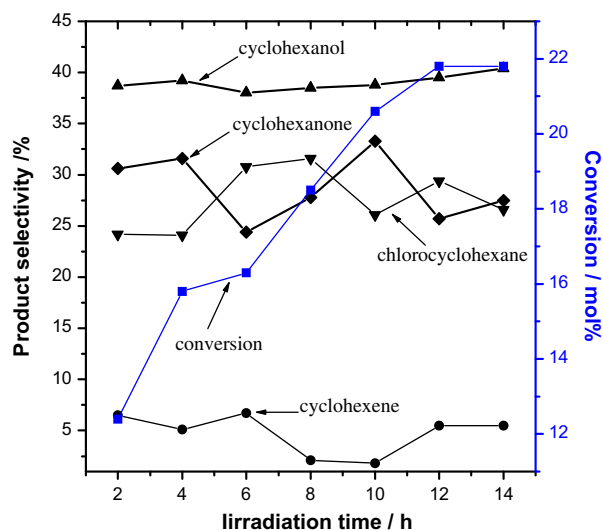


Fig. 7. Effect of irradiation time on the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.08 mol L^{-1})-photocatalyzed reaction.

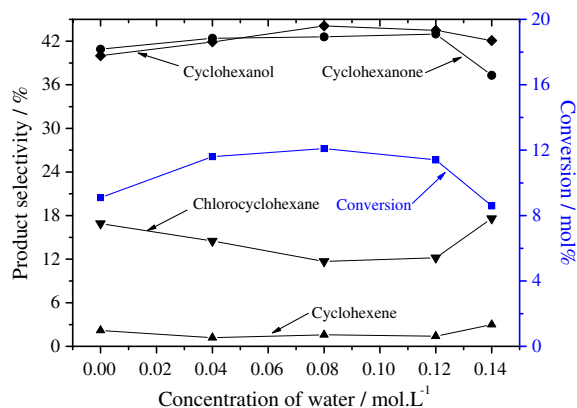


Fig. 8. Effect of H_2O concentration on the CuCl_2 (0.02 mol L^{-1})-photocatalyzed reaction in acetone (irradiation time, 12 h).

$\text{Cu}_2(\text{OH})_3\text{Cl}$ and chlorocyclohexane inevitably occurred in the photo-reaction process.

Fig. 6 illustrates the effect of cyclohexane concentration on the photo-oxidation in MeCN over 0.002 mol L^{-1} concentration of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. When the concentration was reduced from 1.0 to 0.2 mol L^{-1} , the conversion continuously and significantly increased from 10.8% to 24.8%, but the selectivities for the oxygenated and chlorinated products hardly varied. Notably, using low catalyst and substrate concentrations were favorable for improving the conversion and selectivity for the oxygenated products (96–97%), because the formation of chlorocyclohexane (<4% of selectivity) was significantly restrained.

Fig. 7 presents that cyclohexane conversion continuously increased with irradiation time and eventually achieved ca. 21.8% after 12 h. Cyclohexanol selectivity hardly varied with the time, while the selectivities for other products fluctuated in a narrow range.

The effect of the concentration of water on the present photo-oxidation system was investigated using anhydrous CuCl_2 (0.02 mol L^{-1} concentration) in acetone medium. As shown in Fig. 8, an increase in the concentration of water from 0 to 0.08 mol L^{-1} resulted in continuous and slow increases of cyclohexane conversion from 9.1% to 12.1% and selectivity of oxygenated products from 81% to 87%, respectively, with a concomitant decrease in the selectivity of chlorocyclohexane from 17% to 12%. These findings indicate that a suitable amount of water existed in the reaction system, which perhaps plays a positive role in the photocatalysis cycling. On the other hand, the increase in cyclohexanone, and especially cyclohexanol, implies that water partly participates in this photo-oxidation reaction. However, any attempt to further increase the concentration of water resulted in the decreased conversion and selectivity for the oxygenated products. This is likely because the existence of an excess amount of water ($>0.08 \text{ mol L}^{-1}$) can lead to the weakened absorption of CuCl_2 to visible light and decreased solubility of cyclohexane in acetone.

3.2.3. Effect of additive HCl and O_2 pressure

In order to improve the photocatalysis cycling of CuCl_2 , we tried to use concentrated HCl as an additive for the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ -photocatalyzed oxidation, and the results are listed in Table 2. Entries 1 and 3 show that adding 0.2 ml of concentrated HCl to the reac-

Table 2
Influence of adding concentrated HCl and enhancing O_2 pressure on the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ -photocatalyzed oxidation.^a

Entry	HCl (ml)	$\text{P}(\text{O}_2)$ (atm)	Catalyst concn. (mol L^{-1})	Solvent	Conv. (mol%)	TOF^b (h^{-1})	Selectivity of products ^c (%)			
							A	B	C	D
1	0.2	1	0.08	MeCN	36.0	0.38	7	66	21	6
2	–	–	–		26.4	0.28	4	40	40	16
3	0.2	–	–		40.6	0.42	6	50	32	12
4	–	–	–	Acetone	21.8	0.23	5	29	40	26
5	0.1	–	0.01		25.6	2.13	5	38	38	19
6	–	–	–		12.1	1.01	2	13	40	35
7	0.1	–	0.002	MeCN	16.0	6.67	2	23	32	43
8	–	–	–		8.2	3.42	–	3	47	50
9	0.2	–	–		0.8	–	–	63	–	37
10	–	2	0.08	MeCN	24.7	0.26	–	38	25	37
11	–	–	0.002		8.6	3.58	–	2	46	52
12	0.1	–	0.01		31.1	2.59	2	30	38	30
13	0.1	–	0.002	17.8	7.42	–	7	28	65	
14 ^d	–	1	–	–	84.2	–	0.6	2.1	0.2	0.1
15 ^d	–	–	0.08	–	71.2	–	2.0	7.6	4.3	0.9

^a Cyclohexane (5 mmol), catalyst $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, solvent (5 ml), temperature (36–38 °C), time (12 h), using 35 W tungsten–bromine lamp.

^b Turnover frequency based on cyclohexane.

^c A = cyclohexene, B = chlorocyclohexane, C = cyclohexanol, D = cyclohexanone.

^d Adding a radical scavenger BrCCl_3 (0.6 mmol) in photo-oxidation system, the data listed are the content of various components by GC analysis after photoreaction for 12 h, and the content of bromocyclohexane is not listed.

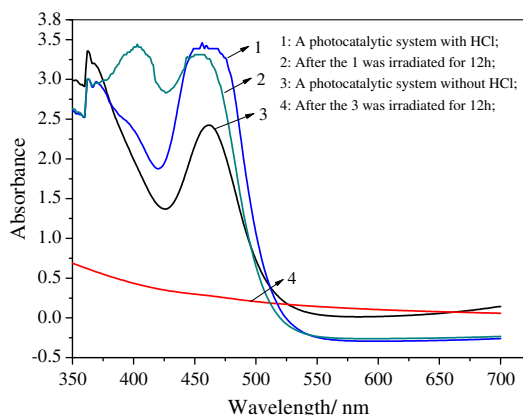


Fig. 9. UV-Vis spectra of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (4×10^{-3} M in acetonitrile)-photocatalyzed oxidation system with and without concentrated HCl (0.2 ml) before and after light irradiation.

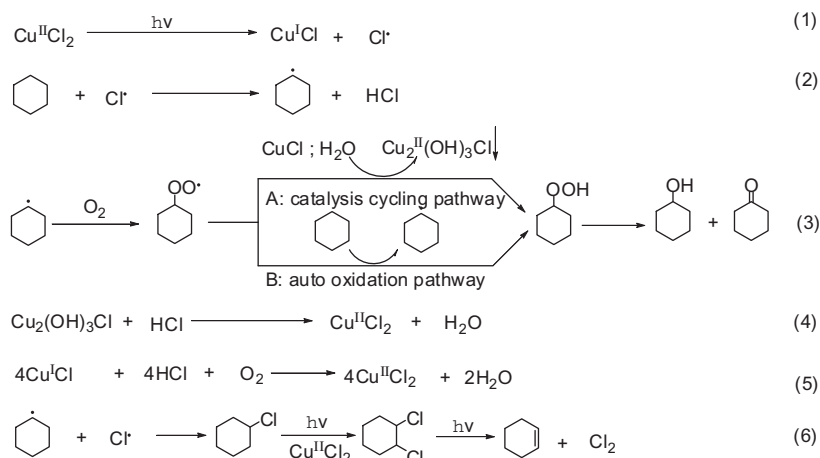
tion system significantly promoted this photocatalytic reaction whether MeCN or acetone was used as solvent, providing much higher turnover frequency (TOF, 038–0.42) and the selectivity for chlorocyclohexane (60–50%) compared to without the additive HCl (entries 2 and 4). Moreover, this promotion effect became more outstanding upon using low catalyst concentration (0.002 and 0.01 mol L^{-1}) in the presence of 0.1 ml of concentrated HCl (entries 5 vs 6 and 7 vs 8). This is likely due to the promoted effect of HCl on the photoredox cycling of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, which can be confirmed by the following facts: (i) The initiated or catalyzed effect of HCl itself on the photo-oxidation was nearly neglected in the absence of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (see entry 9); (ii) The $\text{Cu}_2(\text{OH})_3\text{Cl}$ precipitate mentioned above was not observed in the presence of HCl, in consequence of it to be converted into $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ by HCl; and (iii) the UV-Vis spectral characterization of CuCl_2 -photocatalyzed system shown in Fig. 9 illustrates that the adsorption band of CuCl_2 near 460 nm before and after light irradiation hardly varied in the presence of HCl (curves 1 vs 2), but nearly disappeared in the absence of HCl after 12 h of light irradiation (curves 4 vs 3). Entries 10 and 11 show that slightly increasing O_2 pressure from 1 to 2 atm was nearly invalid in improving photocatalytic activity whether high or low catalyst concentration was used. However, in the presence of 0.1 ml of concentrated HCl, a further promotion effect of increasing O_2 pressure on TOF and cyclohexanone selectivity was observed upon low catalyst concentration (entries 12 and 13). This is likely because Cl atoms and then cyclo-

hexyl radicals produced by light-excited CuCl_2 may be regulated at a very low concentration level in the present conditions, so that increase in O_2 pressure (i.e., concentration) can play roles in improving combination of the cyclohexyl radicals with O_2 molecules and reducing reaction probability of the Cl atoms with cyclohexyl radicals.

3.3. Photocatalytic mechanism

In order to investigate the photocatalysis mechanism of CuCl_2 system, the effect of additive bromo-trichloromethane (BrCCl_3) on the CuCl_2 -photocatalyzed reaction was checked in MeCN. As shown in entry 14 of Table 2, BrCCl_3 as a photosensitizer could initiate the photoconversion of cyclohexane in the absence of CuCl_2 , providing bromocyclohexane (content, 12.8%) and chlorocyclohexane (2.1%) as main products with 15.8% of conversion. But there was only a trace amount of oxygenated products (0.3%) to be detected in this reaction, which is likely because the formation of cyclohexyl hydroperoxide (CyOOH) via an auto oxidation pathway (see Eq. (3) B in Scheme 1), as reported by Hermans and co-workers [45], has a relatively low rate and is easily hampered in the existence of high Br free radicals. In the coexistence of CuCl_2 and BrCCl_3 , the conversion increased to 28.8%, what's more, the content for oxygenated products was improved significantly (5.2%, see entry 15 in Table 2). This indicates that the formation of CyOOH is accelerated in the photoredox cycling of CuCl_2 (see Eq. (3A) in Scheme 1). In addition, a particularly high cyclohexanol to cyclohexanone ratio (4.8) was observed in entry 15, indicating that a reduction of CyOOH to cyclohexanol by CuCl is likely existent, which can lead to a high ratio of cyclohexanol to cyclohexanone.

Based on the results presented here, as well as those in previous studies [21,37], it is apparent that the above data are better explained according to the following reaction pathway (using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ -photocatalyzed system as an example, see Scheme 1). Firstly, visible light-driven electron-transfer process between metal and Cl ions can lead to oxidation of Cl^- ions to Cl atoms and the reduction of $\text{Cu(II)}-\text{Cu(I)}$ ions (Eq. (1)), as confirmed by Cervone and coworkers in the pulsed photolysis experiments of CuCl_2 using a neodymium laser flashing at 473 nm [46]. So the obtained radical species Cl may abstract one H from cyclohexane to form cyclohexyl radical (Cy, see Eq. (2)). Followed by addition of O_2 to the Cy to form a cyclohexyl peroxy radical (CyOO^\bullet), the latter is likely converted to a cyclohexyl hydroperoxide (CyOOH) through a main pathway that the $\text{Cu}^{\text{I}}\text{Cl}$ is oxidized by it to form a $\text{Cu}_2(\text{OH})_3\text{Cl}$ in the participation of water (i.e., catalysis cycling pathway), as pro-



Scheme 1. Proposed photocatalytic mechanism.

posed by Takaki and coworkers [39] and supported by the experimental facts above described; of course, another minor pathway via CyOO abstracting one H atom of cyclohexane to yield a CyOOH and another cyclohexyl radical (i.e., an auto-oxidation pathway) may exist. Finally, the CyOOH can be converted to form the corresponding alcohol and ketone (Eq. (3)), as described by Hermans and coworkers [45]. The precipitate $\text{Cu}_2(\text{OH})_3\text{Cl}$ is easily converted into CuCl_2 in an aqueous HCl medium (see Eq. (4)). Of course, another cycling pathway of CuCl_2 is achieved through O_2 directly oxidizing CuCl in the presence of HCl (Eq. (5)). Undoubtedly, the formation of chlorocyclohexane should be due to the combination of $\text{Cl}\cdot$ with cyclohexyl radicals, and the product, as supported by the above experiment (see entry 22 in Table 1), can be further converted to cyclohexene via a complex and an unverified photoreaction pathway (Eq. (6)). This mechanism shown in Scheme 1 may explain the difference among the photocatalytic performance of other metal salts. It is evident that the Eq. (1) hardly occurs upon the metal salts containing non-halogen anions (CuAc_2 and $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$) or metal cations of low oxidizability such as AlCl_3 , $\text{LaCl}_3\cdot x\text{H}_2\text{O}$, $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, ZnCl_2 , MnCl_2 , and NiCl_2 (see their standard redox potential listed Table 1). CuBr_2 should be easily converted to CuBr and Br atom through Eq. (1), but the Br atom formed is no easy to capture H atom of cyclohexane due to its low activity [47]. $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ with a similar redox potential to $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ shows a poor photocatalysis activity, which is likely due to its weak absorption to visible light and strong hydrolysis in MeCN containing water. Only high-valence metal-containing chlorides that are hardly hydrolyzed easily absorb visible light and achieve redox cycle, such as $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, VOCl_3 , and especially $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, can serve as a good photocatalyst, as supported by the above characterization and reaction results.

4. Conclusion

In summary, we have confirmed that the photocatalytic activity of metal salts is mainly dependent on the following three factors: (i) they are capable of adsorbing visible light through a weak coordination with solvent molecules, (ii) their metal cations have high oxidation valence and easily realize redox cycle, and (iii) their anions easily transfer electrons to metal cations to form active radicals under irradiation. On the other hand, we have developed an efficient and relatively environmentally friendly method to use acetone as a medium for the CuCl_2 -photocatalytic cyclohexane oxidation with dioxygen, and acetone medium is slightly superior to acetonitrile one in the improved selectivity for oxygenated products. Furthermore, we have found that the photocatalysis activity and selectivity for oxygenated products can be significantly improved in the case of using a low catalyst concentration, adding concentrated HCl, and enhancing O_2 pressure. It is anticipated that this photocatalysis system is likely applied in the selective oxidation of other organic compounds with molecular oxygen.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2011.09.034.

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