



Short Communication

Selective decomposition of cyclohexyl hydroperoxide by copper ion-containing quaternary ammonium salts in alkali-free medium



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ABSTRACT

A novel catalytic system composed of quaternary ammonium salts and copper (II) chloride was prepared. The catalyst showed high conversion and selectivity in the decomposition of cyclohexyl hydroperoxide to cyclohexanol and cyclohexanone (K/A oil) at room temperature in alkali-free medium. 93% conversion with 96% selectivity for cyclohexanone and cyclohexanol could be obtained.

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1. Introduction

The liquid-phase autoxidation of cyclohexane is an important industrial process for producing cyclohexanone and cyclohexanol (K/A oil). K/A oil are precursors for caprolactam and adipic acid, which are the building blocks for nylon-6 and nylon-6, 6, respectively.[1] In order to maximize the yield of K/A oil, the industrial process is usually divided into two steps: the first step is cyclohexane oxidation in absence of catalysts at high temperature (160 °C) with low conversion (3.5–4.5%) to maximize the selectivity of cyclohexyl hydroperoxide (CHHP) (60–70%); the second step is the catalytic decomposition of CHHP to K/A oil. Great efforts have been made to develop high active catalysts for the decomposition of CHHP[2–9]. Currently, the most commonly used catalyst is NaOH aqueous containing Co^{2+} in the industrial process. However, this catalyst suffers from economic and environmental drawbacks: (1) low selectivity of K/A oil and a number of ring-opening side reaction products; (2) reaction process consumes a large amount of alkali leading to environmental pollution and increasing costs; (3) not conducive recycling by-product of organic acids in the alkali medium. Thus, it is significant to explore new catalyst for the efficient decomposition of CHHP in alkali-free medium.

Recently, metal ion-containing ionic liquids, especially those based on dialkylimidazolium, N-alkylpyridinium and quaternary ammonium

salts as green catalysts have aroused wide attention in many reactions [10–17]. It is reported that onium salts could promote the homolytic decomposition of CHHP into radicals[18]. Metal ion-containing ionic liquid is a kind of onium cation with metal ion-containing complex as counter anions, which may possess potential applications in the decomposition of CHHP.

In a continuation of our research to develop high-efficiency catalysts for the decomposition of CHHP in alkali-free medium[2–5], herein, copper ion-containing hexadecyl trimethyl ammonium chloride ($[\text{HTA}]_2[\text{CuCl}_4]$) was prepared and applied for the decomposition of CHHP. CuCl_2 could be easily introduced to quaternary ammonium salts via the formation of four-coordinated CuCl_4^{2-} complex. It is found that this catalyst was highly active in the decomposition of CHHP at room temperature.

2. Experimental

2.1. General procedure for the synthesis of $[\text{HTA}]_2[\text{CuCl}_4]$

The copper ion-containing quaternary ammonium salts were prepared as follows: A stoichiometric amount of anhydrous CuCl_2 was added to the anhydrous ethanol solution of quaternary ammonium salts. The reaction mixture was refluxed for 1 h. Then the solvent was evaporated completely, golden solid was obtained. The solid was recrystallized in anhydrous ethanol before use. Calculation for $[\text{HTA}]_2[\text{CuCl}_4]$: C, 58.84%; N, 3.61%; H, 10.84%; Cu^{2+} , 8.26%. Found: C, 58.63%; N, 3.62%; H, 10.57%; Cu^{2+} , 8.44%. Other catalysts were prepared using the same method (Table S1).

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2.2. Synthesis of *n*-heptane solution containing CHHP

Raw material CHHP dissolved in cyclohexane was provided by Liaoyang Synthetic Fiber Co. Ltd. (China). In order to eliminate the influence of cyclohexanol and cyclohexanone that consist in raw material on the results of CHHP decomposition, the raw material was purified before use. Meanwhile, in order to get rid of the phenomenon of cyclohexane oxidation in the process of CHHP decomposition, *n*-heptane was used as alternative solvent. The reaction solution was prepared as follows: the CHHP solution (raw material) was first reacted with NaOH in water, leading to an aqueous solution of the peroxide sodium salt, which was neutralized by NaHCO₃ followed by extraction with *n*-heptane. The organic phase was dried by anhydrous MgSO₄. The solution contains CHHP (0.597 mmol/mL), cyclohexanol (0.006 mmol/mL), cyclohexanone (0.004 mmol/mL), acid and ester (0.011 mmol/mL).

2.3. Decomposition procedure

The reaction was carried out in a 50 mL stainless steel autoclave under magnetic stirring. In a typical procedure, 0.02 g catalyst and 10 mL *n*-heptane solution containing CHHP (0.597 mmol/mL) were added into the reactor. The reaction was conducted at room temperature for 30 min under N₂ atmosphere.

3. Results and discussions

3.1. Characterization of the materials

X-ray diffraction pattern of [HTA]₂[CuCl₄] recrystallized in ethanol was presented in Fig. S1. A series of diffraction peaks of (0 0 *l*; *l* = 2, 4, 6, 8, 10, ...) were observed, suggesting [HTA]₂[CuCl₄] process a high ordered two-dimensional layered perovskite structure.

To further investigate the structure of [HTA]₂[CuCl₄], diffuse reflectance UV–visible spectra (DR UV–vis) were carried out (Fig. 1). Two distinct absorption bands centered at 292 and 402 nm were observed, which could be ascribed to the transition between the Cl (3p) valence band and Cu (4s) conduction band and the transition from the top of the valence band composed of Cl (3p) orbital to the bottom of the Cu (3d) conduction band, respectively. It has been reported that these bands are characteristic absorption of the inorganic sheets of corner-sharing copper chloride octahedral sandwiched with organic layers.[19–22] This indicated that copper chloride was introduced to hexadecyl trimethyl ammonium chloride (HTAC) via the formation of four-coordinated CuCl₄^{2−} complex.

The TGA curve (Fig. S2) showed a drastic weight loss at 235–435 °C, which could result from the decomposition of HTAC. The corresponding weight loss was 83.1%, which was similar to the weight fraction of

organic component in [HTA]₂[CuCl₄] (82.6%). Based on the results of TGA and DR UV–vis, it could be deduced that the molar ratios of HTAC and CuCl₂ is 2, that is consistent with the above-mentioned elemental analysis result, and the counter anion should be CuCl₄^{2−}.

3.2. Catalytic activity

Different catalysts were used for decomposition of CHHP at room temperature. When the reaction was performed without catalyst or with CuCl₂ as catalyst, the decomposition reaction almost did not occur at room temperature (Table 1, entries 1–2). When HTAC was used as catalyst, the conversion of CHHP reached 33% (Table 1, entry 3). It means that quaternary ammonium salt was active in the decomposition of CHHP. Further, [HTA]₂[CuCl₄] showed much higher activity (video in the supporting information), 93% conversion could be obtained under the same conditions (Table 1, entry 7). The CuCl₄^{2−} complex formed by the interaction between copper chloride and quaternary ammonium salts might be able to promote the decomposition of CHHP. In order to display the activity of [HTA]₂[CuCl₄], our former designed catalysts such as cobalt-containing SiO₂-based nanosphere with multi-nanochambers (Co–SiO₂) and α-Co(OH)₂ hierarchical nanoflowers were also tested at room temperature and much lower activity than that of [HTA]₂[CuCl₄] for CHHP decomposition were obtained (Table 1, entries 4–5). Furthermore, industrial catalyst of Co²⁺ in alkali medium was also used to decompose CHHP at room temperature, only 45% conversion and 84% selectivity of K/A oil were obtained. Thus, [HTA]₂[CuCl₄] might be a more appropriate choice for CHHP decomposition from both economic and environmental perspectives.

The influence of different quaternary ammonium cations on the decomposition of CHHP was studied. Octyl trimethyl ammonium chloride, decyl trimethyl ammonium chloride, dodecyl trimethyl ammonium chloride, and tetradecyl trimethyl ammonium chloride combined with CuCl₂ were also effective in the decomposition of CHHP (Table 2). It was found that the activity of catalysts increased with the increase of the length of alkyl chain. The hydrophobicity of this catalyst is enhanced with the length of alkyl chains increasing. We previously showed that the activity in hydrocarbon oxidation could be enhanced by the increase of the hydrophobicity of catalyst [23–26]. Similarly, catalysts with longer alkyl chains were more easily dispersed in the nonpolar solvent, and thus the interaction between CHHP and the catalyst was enhanced.

The effect of other metal on the CHHP decomposition was further studied. The results were summarized in Fig. 2. Mn and Cu showed good performances for CHHP decomposition. While, Ni and Zn showed lower activity than that of Cu. These results may be related to the Lewis acidity and coordination ability of metal ions [27]. The change of the metal ion has a great influence on the catalyst activity. Metal ion might be the major influence factor of our catalytic system.

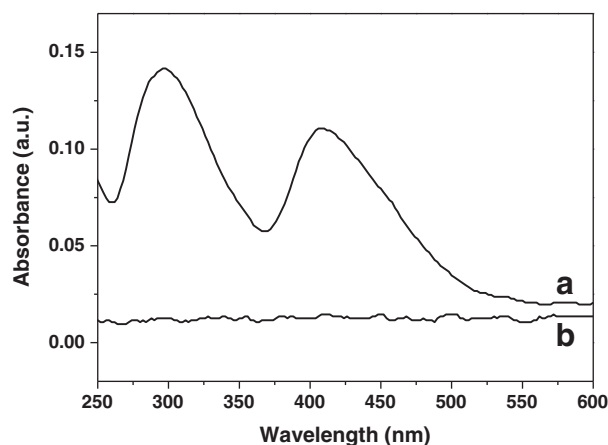


Fig. 1. DR UV–vis spectra of [HTA]₂[CuCl₄] (a) and HTAC (b).

Table 1
Catalytic decomposition of CHHP with different catalysts.^a

Entry	Catalysts	CHHP/ catalyst ^b	Conversion (%)	Selectivity ^c (%)			K/A oil (%)
				A	K	Others	
1	none	–	trace	–	–	–	–
2	CuCl ₂	40	trace	–	–	–	–
3	HTAC	93	33	57	38	5	95
4	Co(OH) ₂	27	24	61	34	5	95
5	Co–SiO ₂	478	18	65	29	6	94
6	Co + NaOH ^d	176000	45	48	36	16	84
7	[HTA] ₂ [CuCl ₄]	231	93	59	37	4	96

^a Reactions were carried out with 0.02 g catalyst in 10 mL *n*-heptane solution containing cyclohexyl hydroperoxide (0.597 mmol/mL) at 25 °C for 30 min.

^b molar ratio of CHHP and catalyst.

^c A, cyclohexanol; K, cyclohexanone; others, mainly adipic acid and esters.

^d Reaction was carried out with 2 mL NaOH aqueous solution (5 wt.%) and 2 ppm Co²⁺.

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