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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.

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 conductive 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 ($[HTA]_2[CuCl_4]$) 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 $[HTA]_2[CuCl_4]$

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 $[HTA]_2[CuCl_4]$: 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 decompostion, 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 $NaHCO_3$ followed by extraction with n-heptane. The organic phase was dried by anhydrous $MgSO_4$. 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 N_2 atmosphere.

3. Results and discussions

3.1. Characterization of the materials

X-ray diffraction pattern of $[HTA]_2[CuCl_4]$ recrystallized in ethanol was presented in Fig. S1. A series of diffraction peaks of (0 0 l; $l = 2, 4, 6, 8, 10, \ldots$) were observed, suggesting $[HTA]_2[CuCl_4]$ process a high ordered two-dimensional layered perovskite structure.

To further investigate the structure of $[HTA]_2[CuCl_4]$, 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 $CuCl_4^{2-}$ 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 $[HTA]_2[CuCl_4]$ (82.6%). Based on the results of TGA and DR UV–vis, it could be deduced that the molar ratios of HTAC and $CuCl_2$ is 2, that is consistent with the above-mentioned elemental analysis result, and the counter anion should be $CuCl_4^{2-}$.

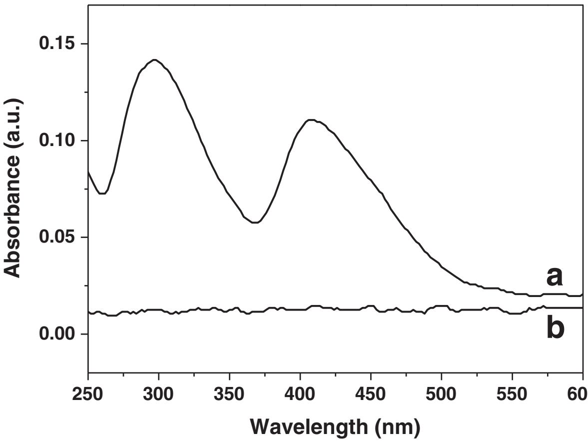

Fig. 1. DR UV–vis spectra of $[HTA]_2[CuCl_4]$ (a) and HTAC (b).

3.2. Catalytic activity

Different catalysts were used for decomposition of CHHP at room temperature. When the reaction was performed without catalyst or with $CuCl_2$ 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, $[HTA]_2[CuCl_4]$ showed much higher activity (video in the supporting information), 93% conversion could be obtained under the same conditions (Table 1, entry 7). The $CuCl_4^{2-}$ 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 $[HTA]_2[CuCl_4]$, our former designed catalysts such as cobalt-containing SiO_2-based nanosphere with multi-nanochambers (Co–SiO_2) and α-$Co(OH)_2$ hierarchical nanoflowers were also tested at room temperature and much lower activity than that of $[HTA]_2[CuCl_4]$ for CHHP decomposition were obtained (Table 1, entries 4–5). Furthermore, industrial catalyst of Co^{2+} 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, $[HTA]_2[CuCl_4]$ 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 $CuCl_2$ 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 alky 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 alky 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.

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 Co^{2+}.

Table 2
Catalytic performance of different quaternary ammonium salts in the decomposition of CHHP.[a]

Catalysts	CHHP/catalyst[b]	Conversion (%)	Selectivity[c] (%)			K/A oil (%)
			A	K	Others	
$[OTA]_2[CuCl_4]$	164	74	49	46	5	95
$[DTA]_2[CuCl_4]$	181	77	50	44	6	94
$[DDTA]_2[CuCl_4]$	198	83	56	40	4	96
$[TTA]_2[CuCl_4]$	215	87	55	41	4	96
$[HTA]_2[CuCl_4]$	231	93	59	37	4	96

[a] Reactions were carried out with 0.02 g of catalyst in 10 mL of n-heptane solution containing cyclohexyl hydroperoxide (0.597 mmol/mL) for 30 min at 25 °C.
[b] molar ratio of CHHP and catalyst.
[c] A, cyclohexanol; K, cyclohexanone; others, mainly adipic acid and esters.

The pathway for CHHP decomposition was studied through real-time *in situ* Fourier transform infrared (FT-IR) spectral measurements (Fig. 3). Before the addition of catalyst, with the background correction (Supporting information), the CHHP revealed intense absorption at 1369 cm^{-1} (vibrational absorption peaks of C–O) could be used to measure the CHHP changes in the reaction process (point-in-time A in Fig. 3). After the addition of $[HTA]_2[CuCl_4]$, CHHP decomposed rapidly and intermediate specie was observed with a broad absorption band at 1680–1600 cm^{-1} (point-in-time B in Fig. 3a). As the reaction proceeded, this peak then disappeared followed by the emerging of vibrational absorption peaks of C–O and C = O in cyclohexanol and cyclohexanone at 1120 and 1725 cm^{-1} respectively. The broad absorption band at 1680–1600 cm^{-1} manifested that new intermediate species formed in the reaction process. Catalyst could rapidly interact with CHHP to form intermediate species, so that accelerating the decomposition of CHHP. Because the reaction proceeds very rapidly, intermediate species are difficult to be separated from the reaction medium. We are currently unable to determine the structure of the intermediate species.

Furthermore, the mechanism of CHHP decomposition was investigated tentatively. When radical inhibitor 2,6-tert-butyl-p-cresol (BHT) was added to the reaction system, the reaction was markedly inhibited and trace amounts of CHHP was decomposed. This indicates that a free radical process might be involved in CHHP decomposition. This result was consistent with other previous research.[18,28,29] What's more, radicals that formed by the homolytic activation of CHHP might be stabilized by BHT radical. The structures of the corresponding free radicals formed in chain initiation were studied by GC-MS preliminarily (Fig. S3). Based on the above results, CHHP decomposition mechanism might be a free radical homolytic mechanism. Through the effect of $[HTA]_2[CuCl_4]$, CHHP acts as radical initiator, which subsequently decomposes mainly into alkyl radical R• and alkoxy radical RO• by the homolytic activation. R• and RO• react very quickly in presence of CHHP to cyclohexanol and cyclohexanone in propagation and termination steps. The detailed mechanism remains to be further studied.

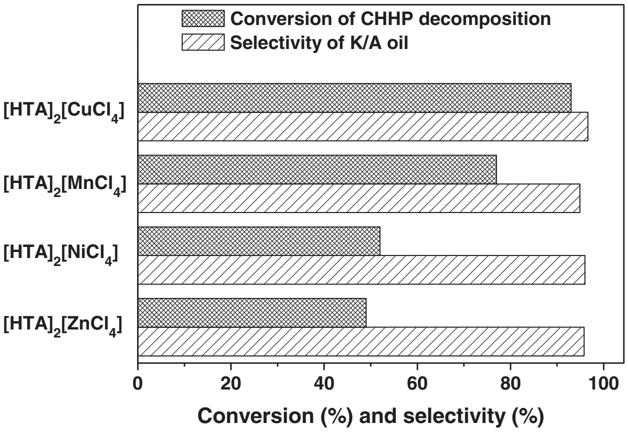

Fig. 2. Catalytic performance of different metal (II) ion-containing catalysts. Reaction conditions: 0.02 g catalyst in 10 mL n-heptane solution containing cyclohexyl hydroperoxide (0.597 mmol/mL) at 25 °C for 30 min.

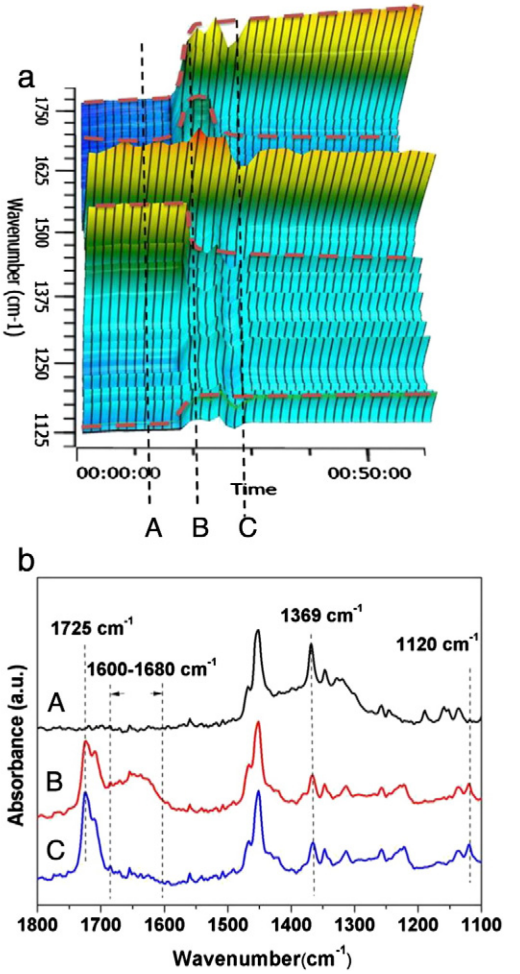

Fig. 3. a) A segment of *in situ* FT-IR for the CHHP decomposition with $[HTA]_2[CuCl_4]$ as catalyst at room temperature (A: no catalyst; B: catalyst was added; C: the end of the reaction). b) FT-IR spectra of point-in-time A, B and C.

In summary, we have developed copper ion-containing quaternary ammonium salts for the catalytic decomposition of CHHP at room temperature in alkali-free medium. Copper chloride is successfully introduced to quaternary ammonium salts *via* the formation of $CuCl_4^{2-}$ complex. The presence of $CuCl_4^{2-}$ complex in the catalytic system is crucial to ensure high efficiency of CHHP decomposition. The relationship between the high activity and structures is now under investigation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.05.022.

References

[1] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R.S. de Cruz, M.C. Guerreiro, D. Mandelli, E.V. Spinace, E.L. Fires, Applied Catalysis A 211 (2001) 1.
[2] X. Zheng, M. Wang, Z.Q. Sun, C. Chen, J.P. Ma, J. Xu, Catalysis Communications 29 (2012) 149.

[3] M. Wang, C. Chen, J.P. Ma, X. Zheng, Q.W. Li, Y.Q. Jin, J. Xu, Journal of Materials Chemistry 22 (2012) 11904.
[4] M. Wang, J.P. Ma, C. Chen, X. Zheng, Z.T. Du, J. Xu, Journal of Materials Chemistry 21 (2011) 12609.
[5] Z.Q. Sun, J. Xu, Z.T. Du, W. Zhang, Applied Catalysis A 323 (2007) 119.
[6] D. Loncarevic, J. Krstic, J. Dostanic, D. Manojlovic, Z. Cupic, D.M. Jovanovic, Chemical Engineering Journal 157 (2010) 181.
[7] R.P. Saint-Arroman, B. Didillon, A. de Mallmann, J.M. Basset, F. Lefebvre, Applied Catalysis A 337 (2008) 78.
[8] A. Ramanathan, M.S. Hamdy, R. Parton, T. Maschmeyer, J.C. Jansen, U. Hanefeld, Applied Catalysis A 355 (2009) 78.
[9] R.P. Saint-Arroman, J.M. Basset, F. Lefebvre, B. Didillon, Applied Catalysis A 290 (2005) 181.
[10] C. Zhong, T. Sasaki, A. Jimbo-Kobayashi, E. Fujiwara, A. Kobayashi, M. Tada, Y. Iwasawa, Bulletin of the Chemical Society of Japan 80 (2007) 2365.
[11] Q.H. Zhang, S.G. Zhang, Y.Q. Deng, Green Chemistry 13 (2011) 2619.
[12] T. Welton, Chemical Reviews 99 (1999) 2071.
[13] J.P. Hallett, T. Welton, Chemical Reviews 111 (2011) 3508.
[14] H. Olivier-Bourbigou, L. Magna, D. Morvan, Applied Catalysis A 373 (2010) 1.
[15] V.I. Parvulescu, C. Hardacre, Chemical Reviews 107 (2007) 2615.
[16] H.B. Zhao, J.E. Holladay, H. Brown, Z.C. Zhang, Science 316 (2007) 1597.
[17] D. Betz, P. Altmann, M. Cokoja, W.A. Herrmann, F.E. Kuhn, Coordination Chemistry Reviews 255 (2011) 1518.
[18] L.J. Csanyi, K. Jaky, Z. Kota, T. Pali, Journal of Molecular Catalysis A: Chemical 209 (2004) 59.
[19] G.S. Li, D.M. Camaioni, J.E. Amonette, Z.C. Zhang, T.J. Johnson, J.L. Fulton, The Journal of Physical Chemistry B 114 (2010) 12614.
[20] T. Sasaki, M. Tada, C. Zhong, T. Kume, Y. Iwasawa, Journal of Molecular Catalysis A: Chemical 279 (2008) 200.
[21] Y.Y. Zheng, G. Wu, M. Deng, H.Z. Chen, M. Wang, B.Z. Tang, Thin Solid Films 514 (2006) 127.
[22] J. Brugger, D.C. McPhail, J. Black, L. Spiccia, Geochimica et Cosmochimica Acta 65 (2001) 2691.
[23] M. Wang, C. Chen, J.P. Ma, J. Xu, Journal of Materials Chemistry 21 (2011) 6962.
[24] C. Chen, J. Xu, Q.H. Zhang, Y.F. Ma, L.P. Zhou, M. Wang, Chemical Communications 47 (2011) 1336.
[25] M. Wang, C. Chen, Q.H. Zhang, Z.T. Du, Z. Zhang, J. Gao, J. Xu, Journal of Chemical Technology and Biotechnology 85 (2010) 283.
[26] C. Chen, L.P. Zhou, Q.H. Zhang, H. Ma, H. Miao, J. Xu, Nanotechnology 18 (2007) 215603.
[27] S. Kobayashi, T. Busujima, S. Nagayama, Chemistry - A European Journal 6 (2000) 3491.
[28] L.J. Csanyi, K. Jaky, I. Palinko, A. Rockenbauer, L. Korecz, Physical Chemistry Chemical Physics: PCCP 2 (2000) 3801.
[29] P.P. Toribio, J.M. Campos-Martin, J.L.G. Fierro, Applied Catalysis A 294 (2005) 290.