



## Selective oxidation of cyclohexane with hydrogen peroxide in the presence of copper pyrophosphate

Ying Du<sup>a,b</sup>, Yonglian Xiong<sup>a</sup>, Jing Li<sup>a</sup>, Xiangguang Yang<sup>a,\*</sup>

<sup>a</sup> Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Science, 5625 Remin Street, Changchun 130022, PR China

<sup>b</sup> Graduate School of the Chinese Academy of Science, Beijing, PR China

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### ABSTRACT

Liquid phase oxidation of cyclohexane was carried out under mild reaction condition over copper pyrophosphate catalyst in  $\text{CH}_3\text{CN}$  using hydrogen peroxide as an oxidant at the temperature between 25 and 80 °C. The copper pyrophosphate catalyst was characterized by means of XRD, FT-IR and water contact angle measurement. It was found that appropriate surface hydrophobicity is the key factor for the excellent performance of the catalyst. In addition, a significant improvement for the cyclohexane conversion in the presence of organic acid was observed.

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### 1. Introduction

Selective oxidation of hydrocarbons with the relatively inert C–H bond to the selective oxygenates is one of the most desirable but challenging reactions [1,2]. The oxidation of cyclohexane is one of the most important reactions in liquid phase oxidation of alkanes due to the large demand for its oxidized products such as cyclohexanol and cyclohexanone which are the important raw materials for the production of adipic acid and caprolactam [3,4]. The present commercial process for cyclohexane oxidation is carried out around 150 °C and 1–2 MPa pressure, nevertheless, only ~4% conversion of cyclohexane and 70–85% selectivity of cyclohexanol and cyclohexanone are obtained. The increased demand for these oxidation products in recent years calls for a more effective catalytic process [5–8]. It means that a higher yield and selectivity of oxygenates should be enhanced in a less polluted process. With respect to the oxidants, hydrogen peroxide is a preferable oxidant because of the simplicity of handling and environmental friendly nature of the co-product (water) in the oxidation reaction [6]. Development of an efficient catalyst for the oxidation of alkanes with hydrogen peroxide as an oxidant is very attractive. But it is very difficult to develop efficient catalyst due to the opposite polarity between two reactants, at which hydrogen peroxide is strong hydrophilic and cyclohexane is strong hydrophobic. Based on Sato's principle, both

hydrogen peroxide and cyclohexane should be adsorbed on the catalyst effectively, therefore, an efficient catalyst should possess moderated hydrophobic surface in order to meet the requirement [9]. Sooknoi and Limtrakul reported more peroxyacetic acid was formed in the reaction using acetic acid as the solvent, and peroxyacetic acid would facilitate the complexation of the framework titanium in terms of relatively higher stability and hydrophobicity [10]. From a mechanistic point of the view, a good catalyst should possess an inherent surface property to meet this reacting condition which is considered to be somewhat of non-polar environment, so the catalyst surface with certain hydrophobicity is favorable to the adsorption of cyclohexane and desorption of the products. Although Antunes' work group reported highly efficient bis-(2-pyridylmethyl)amine Cu(II) complexes catalyst for the oxidation of cyclohexane using hydrogen peroxide or *t*-BuOOH, the catalyst is soluble and unrecoverable by simple filtration [11].

In this regard, many heterogeneous catalysts which have been applied to the oxidation of cyclohexane by using hydrogen peroxide as the oxidant show good activity, such as  $\text{V}_2\text{O}_5\text{-TiO}_2$ , Ce-MCM-41 and nanoporous Mn(II), Co(II), Ni(II) and Cu(II) complexes [12–14]. However, the majority of these reported catalysts are based on silicates–aluminates molecular sieves and their synthesis condition is extreme and time consuming. In addition, leaching of active metal from the catalyst was generally observed in most systems.

Here, we report a copper pyrophosphate catalyst with the moderated hydrophobic surface, which shows the satisfied conversion to the cyclohexane oxidation and selectivity of cyclohexanol and cyclohexanone using hydrogen peroxide in  $\text{CH}_3\text{CN}$  as a solvent.

\* Corresponding author. Tel.: +86 431 85262228; fax: +86 431 85685653.  
E-mail address: [xgyang@ciac.jl.cn](mailto:xgyang@ciac.jl.cn) (X. Yang).

## 2. Experimental

### 2.1. Synthesis of catalyst

Three copper catalysts were prepared according to the procedure described as follows:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (30 mmol),  $\text{Na}_3\text{PO}_4$  (20 mmol),  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  (15 mmol),  $\text{Na}_5\text{P}_3\text{O}_{10}$  (12 mmol) were dissolved in water (100 ml) separately.  $\text{CuSO}_4$  solution was added dropwise into the three sodium salt solutions, and the pH values were of 7, 7–8 and 3–4 in the precipitation, respectively. After precipitation, another 20 h stirring was carried out subsequently. Then, the precipitation were filtered, washed and dried at  $110^\circ\text{C}$  overnight. After calcined at appropriate temperatures three copper catalysts were obtained.

### 2.2. Physic-chemical characterization of catalysts

Powder X-ray diffraction (XRD) patterns were obtained using D/Max-II B diffractometer and  $\text{Cu K}\alpha$  radiation ( $\alpha = 1.5406 \text{ \AA}$ ). The working voltage and current of the X-ray tube were 40 kV and 30 mA. The samples were scanned in the range  $2\theta = 10\text{--}80^\circ$  at a scanning rate of  $3^\circ/\text{min}$ . IR spectra were recorded with a Fourier-transform infrared (FT-IR) spectrometer (BRUKER Vertex 70 FTIR) using the KBr wafer technique for sample preparation. The water contact angles of the three copper catalysts were measured with a Drop Shape Analyzer (DSA10, KRÜSS GmbH, and Hamburg 2001) at room temperature. Water droplets ( $0.2 \mu\text{l}$ ) were dropped carefully onto the catalyst films and the average value of the five measurements at different position of the same sample was adopted in the measuring of contact angle. The above method was in agreement with the method as described somewhere [15]. The specific surface areas of the samples were measured on a Micromeritics ASAP 2012.

### 2.3. Procedure of the selective oxidation reaction and product analysis

In a typical reaction, 50 mg catalyst, 8 mmol cyclohexane, 10 ml solvent (acetonitrile, methanol or dioxane) and 24 mmol hydrogen peroxide (30% aqueous solution) were introduced into a two-neck glass flask equipped with a reflux condenser, after the desired temperature between 25 and  $80^\circ\text{C}$  reached, the reaction system was kept vigorous stirring for 12 h. After the reaction, the product was analyzed by GC (equipped with PEG20W capillary column) and chlorobenzene was used as the internal standard for quantitative determination.

## 3. Results and discussion

### 3.1. Catalyst characterization

The X-ray diffraction patterns of various copper salts after calcined at  $550^\circ\text{C}$  are displayed in Fig. 1, in which three copper phosphates all showed typical crystalline but poor crystallized. In Fig. 1b,  $2\theta = 27.65, 29.81, 34.24, 35.46^\circ$  are attributed to (202), (022), (220), (130), respectively, which is corresponding to copper pyrophosphate (PDF21-880) [16]. The effect of calcined temperature on the crystallization of copper pyrophosphate is depicted in Fig. 2. The samples calcined below  $500^\circ\text{C}$  cannot form the typical crystalline states, whereas the good crystalline state formed at  $550^\circ\text{C}$ . When the catalyst was calcined at  $700^\circ\text{C}$ , the sample was sintered obviously. As shown in Table 1, the specific surface areas of copper pyrophosphate are  $\sim 20 \text{ m}^2 \text{ g}^{-1}$  below  $500^\circ\text{C}$ ,  $\sim 13 \text{ m}^2 \text{ g}^{-1}$  at  $550^\circ\text{C}$  and only  $0.40 \text{ m}^2 \text{ g}^{-1}$  at  $700^\circ\text{C}$ .

The infrared spectra of the samples in the range of  $400\text{--}4000 \text{ cm}^{-1}$  are presented in Fig. 3. The infrared spectra of the

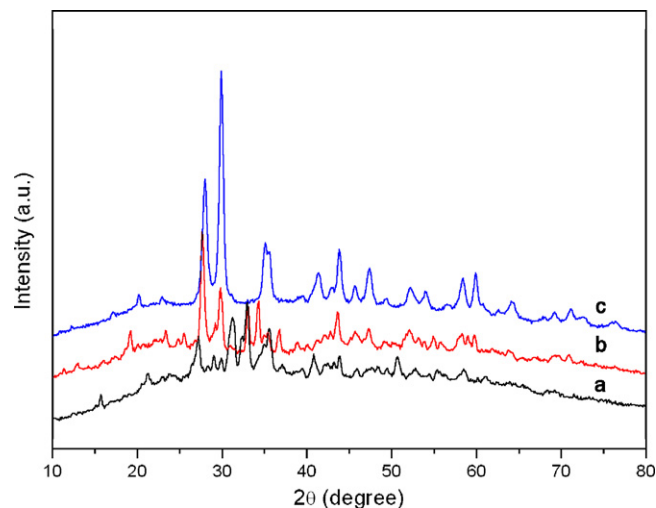


Fig. 1. XRD patterns of the three copper salts: (a)  $\text{Cu}_3(\text{PO}_4)_2$ , (b)  $\text{Cu}_2\text{P}_2\text{O}_7$  and (c)  $\text{Cu}_5(\text{P}_3\text{O}_{10})_2$ .

Table 1

BET surface areas of copper pyrophosphates calcined at different temperatures.

Temperature ( $^\circ\text{C}$ )	300	400	500	550	700
Surface area ( $\text{m}^2 \text{ g}^{-1}$ )	20.8	21.2	13.1	13.0	0.41

samples exhibit a maximum band between  $1000$  and  $1200 \text{ cm}^{-1}$ , which is assigned to the P–O vibrations,  $1067 \text{ cm}^{-1}$  is assigned to  $\text{PO}_3^{-4}$  vibration (Fig. 3a), two bands towards  $937$  and  $760 \text{ cm}^{-1}$  are attributed to P–O–P vibrations and two bands towards  $592$  and  $528 \text{ cm}^{-1}$  are assigned to O–P–O vibrations in case of copper pyrophosphate (Fig. 3b), whereas the bands of  $954, 737, 614$  and  $526 \text{ cm}^{-1}$  are observed in the spectra of copper tripolyphosphate (Fig. 3c) [17–19]. As described above, the hydrophobicity of catalysts is a very important factor in the oxidation of cyclohexane. The water contact angle (WCA) data of the three copper salts are  $0^\circ, 53.5^\circ$  and  $65.2^\circ$  for  $\text{Cu}_3(\text{PO}_4)_2, \text{Cu}_2\text{P}_2\text{O}_7$  and  $\text{Cu}(\text{P}_3\text{O}_{10})_2$ , respectively, as shown in Fig. 4. The results show that both the copper pyrophosphate and copper tripolyphosphate possess the comparative repulsive water ability. The strong hydrophobicity of the copper pyrophosphate and copper tripolyphosphate should be attributed

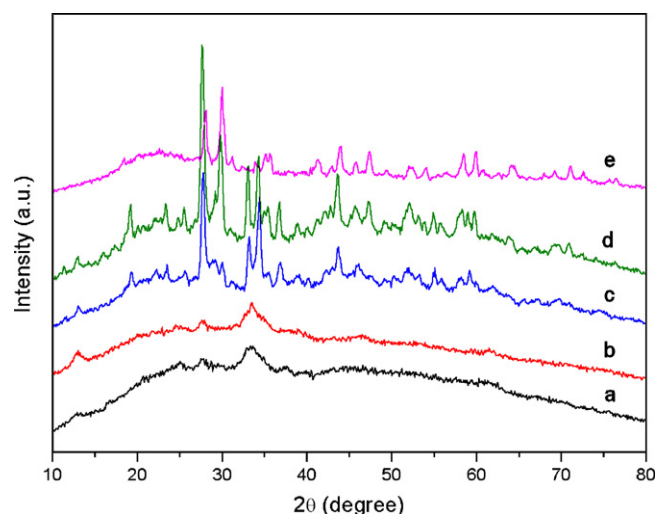


Fig. 2. XRD patterns of copper pyrophosphate catalysts calcined at different temperatures: (a)  $300^\circ\text{C}$ , (b)  $400^\circ\text{C}$ , (c)  $500^\circ\text{C}$ , (d)  $550^\circ\text{C}$  and (e)  $700^\circ\text{C}$ .

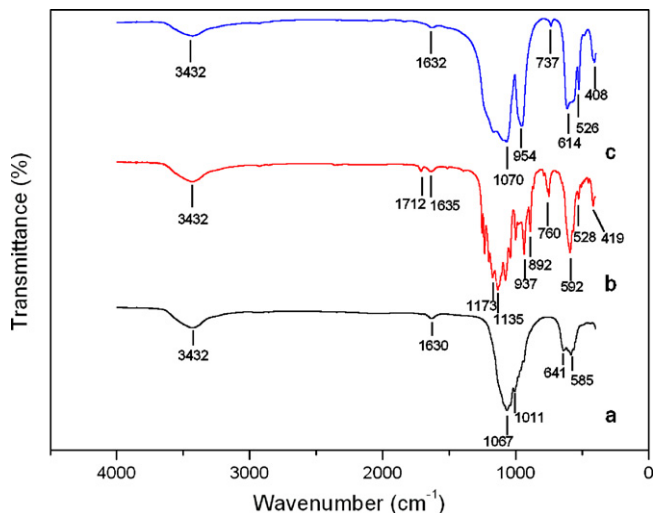


Fig. 3. IR spectra of the three copper salts: (a)  $\text{Cu}_3(\text{PO}_4)_2$ , (b)  $\text{Cu}_2\text{P}_2\text{O}_7$  and (c)  $\text{Cu}_5(\text{P}_3\text{O}_{10})_2$ .

to pyrophosphate ion. On the other hand copper phosphate shows the completely hydrophilicity. It is inferred that copper pyrophosphate should be an efficient catalyst in the oxidation of cyclohexane.

### 3.2. Catalytic activity

In the preliminary experiments, an uncatalyzed oxidation reaction was carried out under the typical reaction conditions in order to evaluate the promotion effect of the reactor wall on the reaction [20]. As shown in Table 2 (entry 1), there are no products formed in the blank reaction.

The following experiments were carried out to check whether the reaction occurred via a heterogeneous-catalysis route. In an

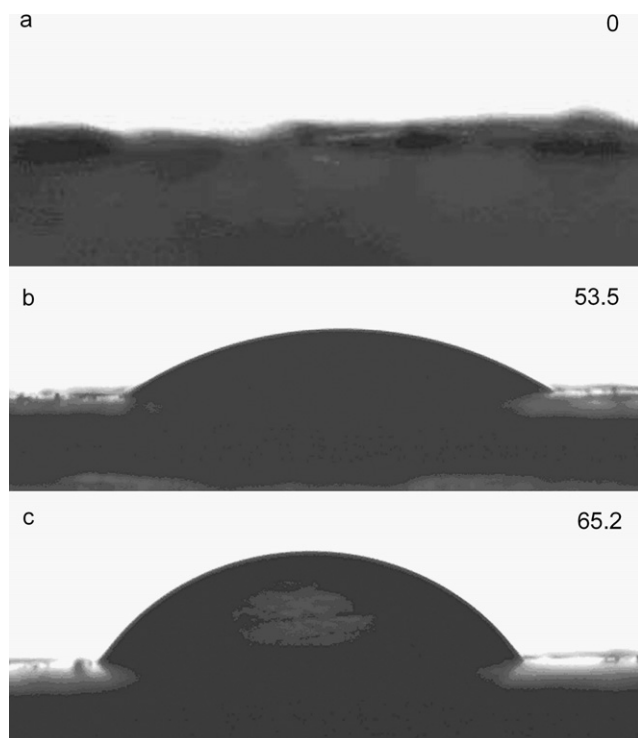


Fig. 4. WCA of the three copper salts: (a)  $\text{Cu}_3(\text{PO}_4)_2$ , (b)  $\text{Cu}_2\text{P}_2\text{O}_7$  and (c)  $\text{Cu}_5(\text{P}_3\text{O}_{10})_2$ .

Table 2

Oxidation of cyclohexane over the three copper salts<sup>a</sup>.

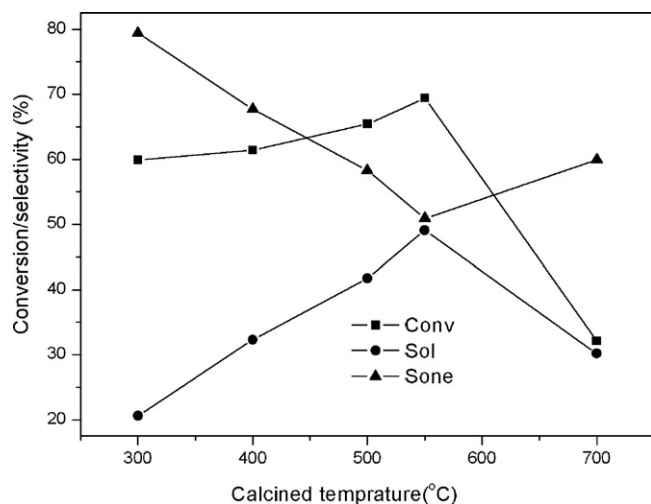
Catalyst	Conversion (%)	Selectivity (%)		
		Cyclohexanol	Cyclohexanone	Cyclohexane
$\text{Cu}_3(\text{PO}_4)_2$	18.6	10.5	49.3	0
$\text{Cu}_2\text{P}_2\text{O}_7$	58.6	36.9	63.1	0
$\text{Cu}_5(\text{P}_3\text{O}_{10})_2$	73.1	12.1	40.7	38.1

<sup>a</sup> Reaction condition: cyclohexane = 8 mmol, cyclohexane/ $\text{H}_2\text{O}_2$  = 1/3, catalyst = 50 mg, acetonitrile = 10 ml,  $T = 65^\circ\text{C}$ ,  $t = 12$  h.

examination reaction, the reaction was carried out in the normal oxidation condition except without cyclohexane for 5 h, then filtrate out the catalyst and cyclohexane with appropriate amount of hydrogen peroxide was added into the reaction system to continue the oxidation reaction. After another 5 h of reaction there were no products formed.

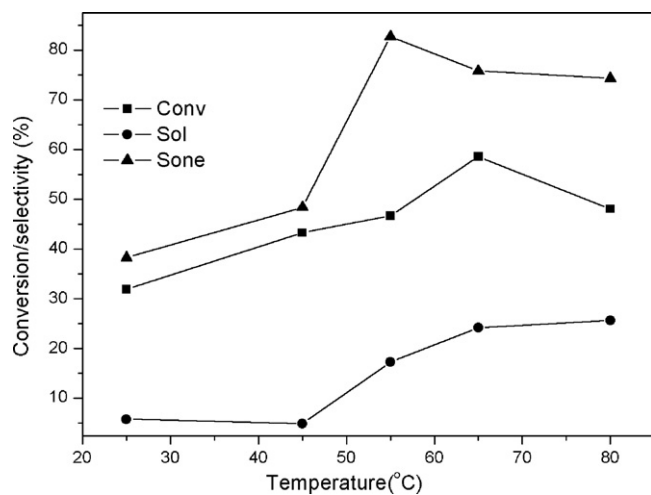
The results of cyclohexane oxidation over three copper salts in  $\text{CH}_3\text{CN}$  solvent are shown in Table 2. It is obvious that satisfactory conversion and selectivity are obtained over copper pyrophosphate. Cyclohexane conversion of 58.6% and ~100% selectivity of cyclohexanol and cyclohexanone should be attributed to the comparative hydrophobicity of copper pyrophosphate, which is favorable to desorb the products, viz., cyclohexanol and cyclohexanone. It is known that cyclohexane (non-polar) is completely hydrophobic and the products cyclohexanol and cyclohexanone (polar) are some hydrophilic in nature. Hence, a certain hydrophobicity of copper pyrophosphate leads to a lower affinity for cyclohexanol and cyclohexanone, which could enhance the desorption of polar products from the active sites as soon as they are formed. At the meanwhile, the moderated hydrophobicity of copper pyrophosphate is also very important, it ensures that both cyclohexane and  $\text{H}_2\text{O}_2$  could be absorbed appropriately and it might be the reason of high conversion of cyclohexane (58.6%) and high selectivity of cyclohexanol and cyclohexanone (~100%). This result is accordant to the idea in the reference [21]. As for copper phosphate, the strong hydrophilicity result in the weak absorption of cyclohexane and hindering the desorption of products, so low sum of selectivity (59.9%) of cyclohexanol and cyclohexanone and the lowest conversion (18.6%) of cyclohexane are observed. When copper tripolyphosphate was used as the catalyst, the relative high conversion was obtained but the total selectivity of cyclohexanol and cyclohexanone reduced to 52.8% as cyclohexene (38.1%) and other by-products (9.1%) were produced simultaneously. Therefore the copper pyrophosphate is the appropriate catalyst for the selective oxidation of cyclohexane among these three phosphate salts in this study.

Fig. 5 shows the effect of the calcined temperatures of catalyst on the oxidation activity. It can be seen that the conversion increases slightly with an increase of the calcined temperature below  $550^\circ\text{C}$ . The conversion reaches the maximum at  $550^\circ\text{C}$  though the specific surface area of the catalyst is smaller than that of copper pyrophosphate calcined at  $400^\circ\text{C}$ , which may be attributed to the perfect crystalline state of the catalyst formed at  $550^\circ\text{C}$  (Fig. 2b). Above results indicate that the BET surface area is not the dominating factor for the catalytic activity. However, a significant decrease of conversion was observed using the catalyst calcined at  $700^\circ\text{C}$  and at the same time unknown products (~10%) were obtained. The catalytic reaction could be hindered by the reduction of catalyst surface due to the sintering under high temperature, but a certain degree of decomposition of copper pyrophosphate cannot be ruled out though it is difficult to be identified by the results of XRD in Fig. 2. So the optimum calcined temperature should be about  $550^\circ\text{C}$  for cyclohexane oxidation.



**Fig. 5.** Effect of the copper pyrophosphate catalysts calcined at different temperatures on the oxidation of cyclohexane: conversion of cyclohexane (■), selectivity of cyclohexanol (●), selectivity of cyclohexanone (▲). Reaction condition: cyclohexane = 8 mmol, cyclohexane/H<sub>2</sub>O<sub>2</sub> = 1/3, catalyst = 50 mg, acetonitrile = 10 ml, T = 65 °C, t = 12 h.

The effect of reaction temperature on the oxidation activity is shown in Fig. 6. It is found that an increase of the conversion and the total selectivity of the cyclohexanol and cyclohexanone with the increase of the reaction temperature from 25 to 65 °C using acetonitrile as the solvent. The total selectivity of the cyclohexanol and cyclohexanone is relatively low under the temperature of 45 °C (Fig. 6). When the temperature increases to 55 °C, ~100% selectivity of cyclohexanol and cyclohexanone is obtained. At higher temperature e.g. 65 °C, the maximum conversion (58.6%) with ~100% selectivity of cyclohexanol and cyclohexanone is achieved. However, the conversion decreases to 48.1% with the reaction temperature further increasing to 80 °C. It is proposed that there would be more self-decomposition of hydrogen peroxide at higher temperature and result in a relatively lower conversion. The above data indicates that the competition between the product and by-product occurs above 65 °C. Hence, the reaction temperature higher than the optimum is in favor of by-production formation in addition to



**Fig. 6.** Effect of the reaction temperatures on the oxidation of cyclohexane over the copper pyrophosphate catalyst: conversion of cyclohexane (■), selectivity of cyclohexanol (●), selectivity of cyclohexanone (▲). Reaction condition: cyclohexane = 8 mmol, cyclohexane/H<sub>2</sub>O<sub>2</sub> = 1/3, catalyst = 50 mg, acetonitrile = 10 ml, T = 25–80 °C, t = 12 h.

**Table 3**  
Effect of the solvents on cyclohexane oxidation over copper pyrophosphate<sup>a</sup>.

Solvent	Conversion (%)	Selectivity <sup>b</sup> (%)
Methanol	~3	~100
1,4-Dioxane	Little	–
Acetonitrile	58.6	~100

<sup>a</sup> Reaction condition: cyclohexane = 8 mmol, cyclohexane/H<sub>2</sub>O<sub>2</sub> = 1/3, catalyst = 50 mg, solvent = 10 ml, T = 65 °C, t = 12 h.

<sup>b</sup> Cyclohexanol + cyclohexanone.

the self-decomposition of hydrogen peroxide. Thus 65 °C should be suitable for the present selective oxidation of cyclohexane.

The solvent usually determines the medium polarity and plays an important role in the activity of catalysts [22], but the main action of solvent is still to facilitate homogeneity of immiscible liquid phase. For example, many solvents have been investigated in the liquid phase oxidation of olefins and alcohols using titanium-containing zeolites as the catalyst [9,23], but no significant effect of solvent has been reported for cyclohexane oxidation. As listed in Table 3, acetonitrile is almost a perfect solvent for cyclohexane oxidation over copper pyrophosphate. Using 1,4-dioxane or methanol as a solvent, a low conversion of cyclohexane is observed. But cyclohexane conversion is enhanced obviously in acetonitrile as a solvent. In this study, it is believed that the solvent acetonitrile acted as a ‘media’ serving homogeneity for the liquid phase. Cyclohexane and hydrogen peroxide are mutual dissolved in acetonitrile and the reaction products, viz., cyclohexanol and cyclohexanone are not only soluble in the reaction mixture but also can be displaced from the surface of catalyst as they formed.

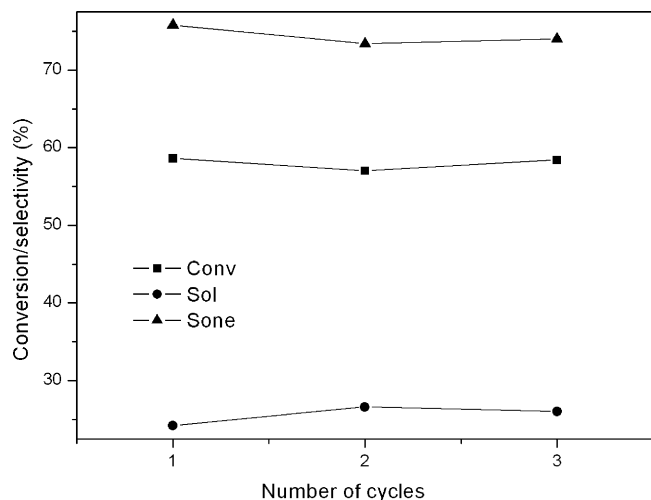
As known, enhancement of the activity by acetic acid in the oxidation of cyclohexane has been reported in the literatures [10,24]. In the media of acetic acid, hydrogen peroxide is more stable and diminishes the self-decomposition by forming peroxyacetic acid. At the same time, as peroxyacetic acid is more hydrophobic than the hydrogen peroxide, it acts as a “soft” ligand, favoring to the oxidation of cyclohexane [10]. A remarkable increase of activity was achieved when 2.5 mmol organic acid was added into the reaction system. The capability of the increase of conversion by the addition of citric acid is higher than that of acetic acid (as shown in Table 4). A conversion of 93.3% is obtained when citric acid is added, which is the highest conversion in this study. Activation of hydrogen peroxide by citric acid in acidic solution has been reported in [25]. In our study, it is proposed that the formation of peroxyacetic acid just like the formation of peroxyacetic acid. Citric acid is also a tribasic acid and reacts with heavy metals spontaneously, therefore, an effect of diminishing the self-decomposition of hydrogen peroxide can be expected.

To check the stability and recycling ability of the catalyst, the used catalyst was separated from the reaction mixture and dried at 110 °C, then recycling experiments were performed under the typical reaction conditions. As given in Fig. 7 the results show that the catalyst is still active after three times without any appreciable loss of conversion and selectivity.

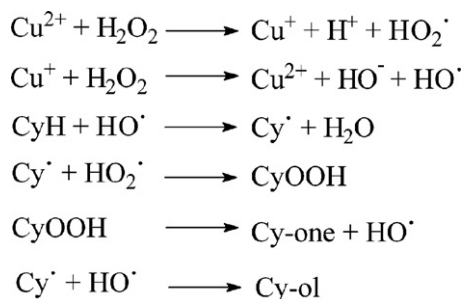
**Table 4**  
Results of cyclohexane oxidation in the presence of organic acids<sup>a</sup>.

Acid	Conversion (%)	Selectivity (%)			
		Cyclohexanol	Cyclohexanone	Cyclohexane	Other
Acetic acid	77.9	12.5	46.1	28.6	12.8
Citric acid	93.3	13.5	33.3	38.4	14.8

<sup>a</sup> Reaction condition: cyclohexane = 8 mmol, cyclohexane/H<sub>2</sub>O<sub>2</sub> = 1/3, catalyst = 50 mg, acetonitrile = 10 ml, 2.5 mmol organic acid (acetic acid, citric acid), T = 65 °C, t = 12 h.



**Fig. 7.** Recycling studies of the oxidation of cyclohexane over copper pyrophosphate: conversion of cyclohexane (■), selectivity of cyclohexanol (●), selectivity of cyclohexanone (▲). Reaction condition: cyclohexane = 8 mmol, cyclohexane/H<sub>2</sub>O<sub>2</sub> = 1/3, catalyst = 50 mg, acetonitrile = 10 ml, T = 65 °C, t = 12 h.



**Scheme 1.** A possible mechanism of the oxidation of cyclohexane over copper pyrophosphate catalyst.

In order to study the mechanism, iodine as an inhibitor for radical reaction was added into the reaction system, at last, no product was found. It is inferred that the reaction is processing by the radical route and a possible mechanism was proposed in Scheme 1 [26–28].

## 4. Conclusions

Copper pyrophosphate, possessing comparatively hydrophobicity, is very efficient to the oxidation of cyclohexane in acetonitrile solvent at 65 °C. The conversion of cyclohexane is 58.6%, the selectivity of cyclohexanol and cyclohexanone was almost 100%. The conversion of cyclohexane is promoted by the addition of organic acid in the reaction mixture.

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