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Synthesis and Structure of Copper Hydroxyphosphate and Its High Catalytic Activity in Hydroxylation of Phenol by H_2O_2

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A complex oxide of $Cu_2(OH)PO_4$ has been successfully synthesized by the hydrothermal method, and its structure was investigated by X-ray analysis. It crystallizes in the orthorhombic space group of *Pnnm* with $a = 8.058(2)$, $b = 8.393(2)$, and $c = 5.889(2)$ Å. Furthermore, the sample was characterized by thermal analysis (DTA and TG), and these results indicated that the sample was stable below 650°C. After calcination at 850°C, $Cu_2(OH)PO_4$ was dehydrated to form $Cu_4O(PO_4)_2$. The sample isotherm for N_2 showed that there wre no micropores or mesopores, and the surface area was only at 1.4 m^2/g when the particle size of the sample was 150 μm. Moreover, when this sample was used as a catalyst for phenol hydroxylation by H_2O_2, the catalytic data showed high activity, which was comparable to that of TS-1. Various factors that influence this catalytic reaction, such as the solvent, reaction temperature, reaction time, catalyst size, catalyst amount, molar ratio of phenol to H_2O_2, and mode of H_2O_2 addition, were investigated intensively. Additionally, this catalytic reaction was characterized by electron spin resonance (ESR), and it was found that on the $Cu_2(OH)PO_4$ catalyst hydroxyl radicals possibly resulting from Cu^{2+} and H_2O_2 were important intermediates for formation of catechol and hydroquinone from hydroxylation phenol. © 2001 Academic Press

Key Words: **complex oxide; $Cu_2(OH)PO_4$; phenol hydroxylation; hydrogen peroxide; electron spin resonance (ESR).**

INTRODUCTION

Catalytic hydroxylation of phenol, as an important industrial reaction for production of fine chemicals, has been investigated recently (1–9), and a large amount of research is focused on microporous and mesoporous materials because of their large surface area with high metal dispersion. As typical catalysts, microporous and mesoporous titanosilicates with large surface area (300–1200 m^2/g) are effective catalysts for phenol hydroxylation in the presence of hydrogen peroxide (1–9).

Although these titanosilicates have been investigated extensively, some disadvantages of these catalysts will limit their applications as tools for oxidation reactions in organic chemistry. For examples, the synthesis of microporous and mesoporous titanosilicates is somewhat complicated by the need to avoid precipitation of TiO_2 as a separate phase, which often acts as a catalyst poison in the subsequent oxidation reactions by hydrogen peroxide; the small crystal size (0.1–10 μm) of microporous and mesoporous titanosilicates makes it difficult to separate catalysts mixed with the reaction products; the small pore size of microporous titanosilicates restricts their use in oxidation reactions for larger organic molecules (1–8); the low hydrothermal stability of mesoporous MCM-41 (9) will strongly influence the life of the mesoporous catalyst. Thus, new materials with much higher reaction activity have always been sought.

On the other hand, materials with small surface area have not been widely studied as oxidation catalysts yet; they were usually considered to suffer low catalytic conversion or to be inactive as catalysts in oxidation reactions (1–10).

More recently, we found that a series of complex oxides such as V–Zr–O and Cu–Bi–V–O with small surface area at 1.0–4.0 m^2/g were active for phenol hydroxylation in the presence of H_2O_2 (11–13). Additionally, we observed that $Cu_2(OH)PO_4$ was better than V–Zr–O and Cu–Bi–V–O, and its catalytic activity has been reported as a research letter (14). Here we show detailed results on this novel catalyst, $Cu_2(OH)PO_4$.

EXPERIMENTAL

Materials

Ethylenediamine ($H_2NCH_2CH_2NH_2$), phosphoric acid (H_3PO_4, 85 mass%), copper acetate ($CuAc_2$), $CuCl_2$, CuO, Na_3PO_4, phenol, and hydrogen peroxide (H_2O_2 30%) of analytical reagent grade were from Beijing Chemical Co. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) of G.R. purity was purchased from Aldrich Chemical Co.

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Preparation of $Cu_2(OH)PO_4$

The copper hydroxyphosphate of nominal composition $Cu_2(OH)PO_4$ was hydrothermally synthesized using $H_2NCH_2CH_2NH_2$, H_3PO_4, and $CuAc_2$ as starting materials with molar ratio of 1.0 $H_2NCH_2CH_2NH_2$: 2.9 H_3PO_4 : 1.0 $CuAc_2$: 25 H_2O. At first, $CuAc_2$ was added into water with stirring for 30 min, followed by addition of H_3PO_4. After the mixture was stirred for 1.5 h, $H_2NCH_2CH_2NH_2$ was added, and pH of the mixture was controlled between 5–6. The mixture was then stirred until it became homogeneous. Finally, the gel was sealed in a Teflon-lined stainless steel autoclave and heated in an oven for 3 days at 150°C. The crystalline product was filtered, washed with distilled water, and dried at ambient temperature. The final product with very controlled crystal size (50–500 μm) was obtained.

Smaller crystal sizes (average size) of 5 and 15 μm were prepared by mechanically grinding $Cu_2(OH)PO_4$ catalyst with a crystal size of 150 μm at room temperature for 10 and 35 min, respectively.

Characterization

The samples in this study were characterized by X-ray diffraction (XRD), scanning electron micrography (SEM), adsorption for N_2, water, and hexane, temperature-programmed desorption of ammonia (TPD-NH_3), differential thermal analysis (DTA), thermogravimetry analysis (TGA), and X-ray structural analysis of a single crystal.

The XRD patterns were recorded using a Rigaku D/Max IIIA diffractor with Cu$K\alpha$ radiation at room temperature in the range of 4–40°. A Hitachi X-650 scanning electron microscope was used for measurement of crystal size. DTA and TGA were performed on a Perkin-Elmer DTA 1700 analyzer and TGA-7PC analyzer with a heating rate of 10°C/min, respectively. The surface area of the catalyst was measured with nitrogen adsorption methods (BET) by using a Micromeritics ASAP 2010M at −196°C, and the adsorption isotherms for water and hexane were carried out using the Cahn-2000 microbalance at room temperature (25°C). The sensitivity of the microbalance was ±0.1 μg. Structural data on a single crystal of the sample were collected with a Siemens CCD Smart 1000 with Mo$K\alpha$ radiation. All computations were carried out using the SHELXTL program (version 5.0) (15). Electron spin resonance (ESR) spectroscopy was recorded at room temperature using a Brucker ER 200D-SRC instrument at a frequency of 9.77 GHz, a modulation frequency of 100 KHz, a field modulation intensity of 1.25 Gpp, a microwave power of 6.5 mW, a time constant of 500 ms, a scan range of 100 G, and a mild range of 3480 G. Temperature-programmed desorption spectra of ammonia (TPD-NH_3) curves were performed in the range of 120–600°C, increasing at a rate of 15°C/min. The adsorption of ammonia on the sample was performed at room temperature, followed by removal of ammonia by physical adsorption at 120°C for 1 h in flowing pure nitrogen.

Catalytic Phenol Hydroxylation

Phenol hydroxylation experiments were run in a 50-ml glass reactor and stirred with a magnetic stirrer. In a standard run, 20.4 mmol of phenol, 0.08 g of catalyst, and 15 ml of solvent were mixed, followed by addition of 6.8 mmol of H_2O_2 (30% aqueous) (molar ratio of phenol/$H_2O_2 = 3.0$). After reaction for 4 h at 80°C, the products hydroquinone (HQ), catechol (CAT), and 1,4-benzoquinone (BQ) were analyzed by gas chromatography (Shimadzu GC-9A) with a flexible quartz capillary column coated with OV-17. The initial programmed temperature was at 140°C, the final temperature was at 186°C, and the injector temperature was 280°C. The amount of tar was determined by evaporation *in vacuo*.

ESR Spectroscopy

ESR spectra were recorded at room temperature; DMPO was chosen as a spin-trapping reagent. To determine the relative intensity of radicals quantitatively, all reagents in this study were calculated, and a quartz tube with a diameter of 1 mm was used. After the reactants were added into the reaction quartz tube, the ESR spectra were measured.

RESULTS AND DISCUSSION

Structure of $Cu_2(OH)PO_4$

Copper hydroxyphosphate with some impurities was first observed in mineral products (16), and there is no report of hydrothermal synthesis of this sample yet.

The XRD pattern (Fig. 1a) of as-synthesized copper hydroxyphosphate showed several obvious peaks at 15.2°, 18.5°, 30.0°, 34.2°, and 37.3° in the range of 4–40°, which were similar to those of Libethenite mineral (16). Single-crystal diffraction data were collected using a Siemens CCD Smart 1000 with Mo$K\alpha$ radiation. All computations were carried out using the SHELXTL program (Version 5.0) (15). The structure was resolved by direct method and refined by full-matrix least squares to $R = 0.043$ and $R_w = 0.360$. The deep green copper hydroxyphosphate crystallized in the orthorhombic space group of *Pnnm* with $a = 8.058(2)$, $b = 8.393(2)$, and $c = 5.889(2)$ Å. The structure consisted of a PO_4 tetrahedron, a $Cu(1)O_5$ trigonal bipyramid, a $Cu_{(2)}O_6$ octahedron, and a OH group between two Cu species, in which oxygen atoms were shared with each other, but no P–O–P chains (Fig. 2). In the $Cu(1)O_5$ trigonal bipyramid, two oxygen atoms were close to the Cu atom, giving Cu–O distances that averaged 1.932 Å, and three oxygen atoms were far from the Cu atom, giving Cu–O distances that averaged 2.05 Å. In the $Cu(2)O_6$ octahedron, four oxygen

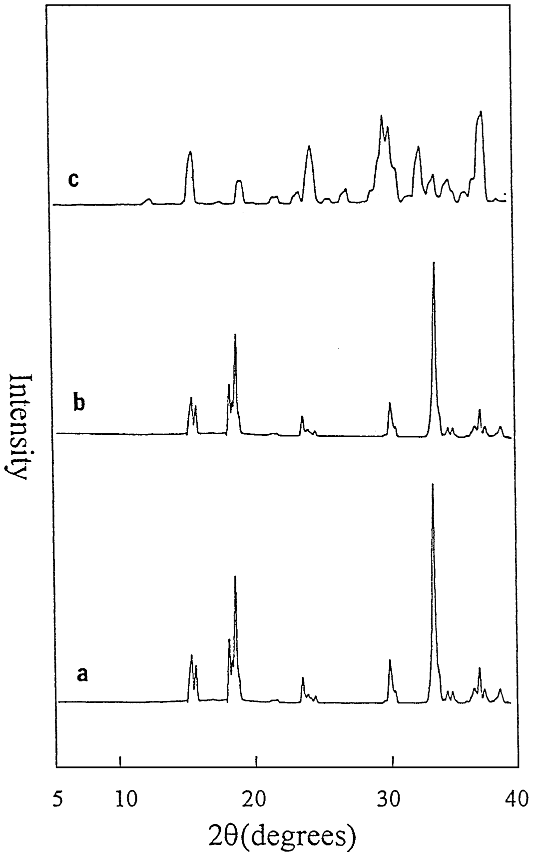

FIG. 1. XRD patterns of (a) $Cu_2(OH)PO_4$, (b) calcination of $Cu_2(OH)PO_4$ at 550°C for 2 h, and (c) $Cu_4O(PO_4)_2$ samples.

atoms were close to the Cu atom, giving Cu–O distances that averaged 1.970 Å, and two oxygen atoms were far from the Cu atoms, giving Cu–O distances that averaged 2.399 Å. As a result, the $Cu(2)O_6$ octahedron became longer due to John–Teller distortion (17). In the PO_4 tetrahedron, P–O distances varied from 1.517–1.568 Å (average 1.538 Å), and O–P–O angles were within range 106.6–110.5°, which suggested that the tetrahedron was highly symmetrical. The structural parameters for this sample are summarized in Table 1.

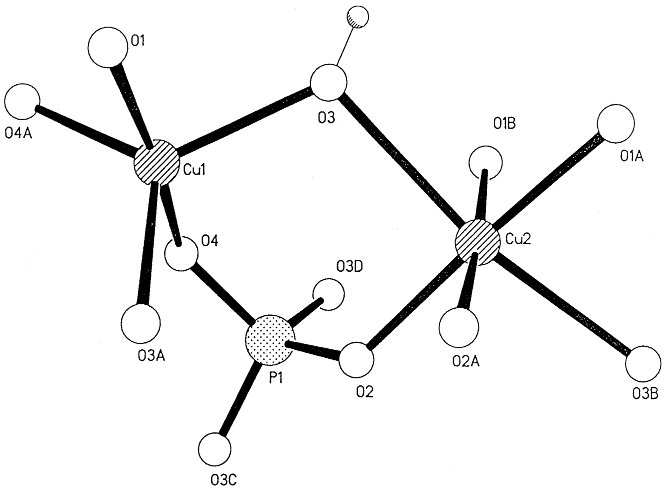

FIG. 2. Asymmetric unit of the $Cu_2(OH)PO_4$ sample.

TABLE 1

Crystallographic Data of Copper Hydroxyphosphate

Formula	$Cu_2(OH)PO_4$
Formula weight	345.69
Crystal system	Orthorhombic
Space group	*Pnnm*
Lattic parameters	$a = 8.058(2)$ Å, $b = 8.393(2)$ Å, $c = 5.889(2)$ Å, $\alpha = 90°$ $V = 398.28(14)$ Å^3
Z value	2
D_c	2.883
Radiation	$MoK\alpha(\lambda = 0.71073$ Å$)$
Scan range	3.51°–25°
Scan type	ω
Independent reflections	386
Observed ($I > 2\sigma(I)$)	386
Structure solution	Direct method
Refinement	Full-matrix least-squares
Residuals R; R_w	0.0428; 0.3601
S	1.175
$(\Delta\rho)_{max}$	1.263–1.258

Characterization of $Cu_2(OH)PO_4$

The DTA curve of the $Cu_2(OH)PO_4$ showed a peak at 670°C, which was assigned to the change in sample structure, and below 650°C there were no obvious peaks. Correspondingly, TG analysis showed that there was no weight loss in the range of 25–650°C, and when the temperature was over 650°C, there was an obvious weight loss, which was assigned to dehydration of the sample. These results suggested that $Cu_2(OH)PO_4$ was thermally stable from 25–650°C, and when the temperature was over 650°C the sample structure changed.

After calcination at 850°C for 6 h, the sample XRD pattern gave peaks quite different from those of the as-synthesized sample, appearing at $2\theta = 15.6°$, 19.5°, 24.7°, 30.5°, 33.0°, and 38.2°, respectively, as shown in Fig. 1c. These results suggested formation of a new phase assigned to $Cu_4O(PO_4)_2$, which resulted from dehydration of $Cu_2(OH)PO_4$ (18).

The particle size of the sample was estimated by SEM measurement, and SEM results indicated that the particle size was very uniform and the crystal size could be controlled at 50–500 μm by changing the synthesis conditions.

N_2 adsorption over $Cu_2(OH)PO_4$ catalyst showed a very low yield, and the BET surface area was only 1.4 m^2/g, indicating that there were no micropores or mesopores. Adsorption of water over the $Cu_2(OH)PO_4$ also showed very

TABLE 2

Catalytic Activities and Selectivity in Phenol Hydroxylation by H_2O_2 over Various Catalysts[a]

Catalyst	Phenol conv. (%)	H_2O_2 eff. conv.[b] (%)	Product selectivity (%)[c] BQ	CAT	HQ
Na_3PO_4	Inactive	—	—	—	—
$CuCl_2$	7.5	28.1	25.1	35.3	39.6
CuO	7.9	30.5	11.8	47.3	40.9
$Cu_4O(PO_4)_2$	11.2	39.6	19.3	43.5	37.2
$Cu_2(OH)PO_4$	28.3	84.6	1.1	52.2	46.7
TS-1[d]	27.0	82.0	1.0	49.0	50.0

[a] Reaction conditions: water as a solvent, reaction temperature 80°C, phenol/H_2O_2 = 3/1 (molar ratio), reaction time 4 h, catalyst/phenol = 5% (weight ratio).

[b] The efficiency conversion of H_2O_2 was calculated as follows: H_2O_2 eff. conv. = 100 × H_2O_2 (mol) consumed in formation of diphenols and benzoquinone/total H_2O_2 (mol) added.

[c] CAT = catechol, HQ = hydroquinone, and BQ = benzoquinone. The product of tar is not included, and the product selectivity is CAT (or HQ or BQ)/(CAT + HQ + BQ).

[d] Reaction conditions (26): TS-1 with Ti/(Ti + Si) = 0.091, acetone as a solvent, reaction temperature 57°C, phenol/H_2O_2 = 3 (molar ratio), reaction time 6 h, and catalyst/phenol (g/g) = 10%.

low yield, at 0.008 g/g. In contrast, the sample could not adsorb hexane. Furthermore, the SEM measurements indicated that the particle size of $Cu_2(OH)PO_4$ catalyst used was close to 150 μm.

Moreover, the TPD-NH_3 curve of $Cu_2(OH)PO_4$ showed that there was no chemical adsorption, suggesting that this material was not acidic. Such a phenomenon was similar to that of TS-1.

Catalytic Phenol Hydroxylation

Comparison of catalytic activity over various samples. Catalytic activities and selectivities in phenol hydroxylation by H_2O_2 over various samples of Na_3PO_4, $CuCl_2$, $Cu_4O(PO_4)_2$, CuO, and $Cu_2(OH)PO_4$ are presented in Table 2. Na_3PO_4 was catalytically inactive. A series of catalysts containing copper species such as $CuCl_2$, CuO, $Cu_4O(PO_4)_2$, and $Cu_2(OH)PO_4$ were catalytically active, giving conversions of 7.5–28.3%. These results suggested that copper species might be catalytically active sites in phenol hydroxylation by H_2O_2, and similar results have been reported by Wu *et al.* before (19–21).

Notably, the catalysts $CuCl_2$, CuO, and $Cu_4O(PO_4)_2$ showed relatively low conversions of 7.5, 7.9, and 11.2% , respectively. However, the activity over $Cu_2(OH)PO_4$ catalyst was very high, giving conversion of 28.3%, which was comparable to that of microporous TS-1 zeolite which was considered as an effective catalyst in hydroxylation of phenol (22, 23). Obviously, the unusual catalytic activity in hydroxylation of phenol on $Cu_2(OH)PO_4$ catalyst could be related to the unique structure of as-synthesized $Cu_2(OH)PO_4$.

The structure of $Cu_2(OH)PO_4$ has been well characterized, and its basic building units were very similar to those of $Cu_4O(PO_4)_2$ prepared from calcination of $Cu_2(OH)PO_4$ (Fig. 1c). Notably, the $Cu_4O(PO_4)_2$ also consisted of CuO_5 and CuO_6 units, but the catalytic activities for the two catalysts were greatly different. The only difference in structure between $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ is the OH species attached on Cu sites (18). On the basis of the large difference in catalytic conversion for $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts (Table 2), we suggest that the OH species attached on Cu sites play an important role in the catalysis.

Interestingly, the surface area of $Cu_2(OH)PO_4$ was very small, and determination of the surface area for used $Cu_2(OH)PO_4$ catalyst showed only 1.4 m^2/g. Since only the sites on the surface can interact with reactants in the catalysis, very high turnover frequency of the $Cu_2(OH)PO_4$ was achieved in this study. At 80°C, the turnover frequency (875 h^{-1}) of the $Cu_2(OH)PO_4$ was comparable to that (7.2 h^{-1}) of TS-1 catalyst (2). This catalytic phenomenon for $Cu_2(OH)PO_4$ catalyst may be related to a reaction mechanism different from that of TS-1 catalyst. To our knowledge, this is the highest frequency of turnover reported for catalytic hydroxylation of phenol catalyzed by reported catalyst materials (1–9).

It is well known that the solvent, reaction temperature, reaction time, catalyst size, catalyst amount, molar ratio of phenol to H_2O_2, and mode of H_2O_2 addition are major factors in phenol hydroxylation, and these factors are systematically investigated in the following sections.

Influence of the solvent. It has been reported the solvents in this reaction have a profound influence on the phenol conversion and the ratio of catechol to hydroquinone over microporous titanosilicalites (24, 25). Table 3 presents a summary of solvent influence in phenol hydroxylation over $Cu_2(OH)PO_4$ catalyst. When acetone and 1,2-dichloroethane were used as solvents, phenol hydroxylation did not occur, even at temperatures up to

TABLE 3

Catalytic Activities and Selectivity in Phenol Hydroxylation by H_2O_2 over $Cu_2(OH)PO_4$ Catalyst with Various Solvents[a]

Solvent	Temperature (°C)	Phenol conv. (%)	Product selectivity (%) BQ	CAT	HQ
Water	80	28.3	1.1	52.2	46.7
Acetonitrile	60	8.9	3.5	60.5	36.0
Acetone	60	Inactive	—	—	—
1,2-Dichloroethane	60	Inactive	—	—	—

[a] Other reaction conditions are the same as those in Table 2.

TABLE 4

Catalytic Activities and Selectivity in Phenol Hydroxylation by H_2O_2 over $Cu_2(OH)PO_4$ Catalyst with Various Amounts of Water[a]

Water amount (ml)	Phenol conv. (%)	Product selectivity (%)			Tar selectivity[b] (%)
		BQ	CAT	HQ	
2.5	26.1	5.5	53.0	41.5	28.6
5.0	25.5	3.7	53.6	42.7	27.4
7.5	25.2	1.7	51.5	46.8	26.5
10	25.0	0.3	50.6	49.1	24.9
15	28.3	1.1	52.2	46.7	19.1
20	24.2	1.4	50.6	48.0	15.9
30	21.0	2.9	51.0	46.1	12.6

[a] Other reaction conditions are the same as those in Table 2.

[b] Tar selectivity specified in Ref. (26).

90°C. In contrast, acetone was the best solvent for hydroxylation of phenol over TS-1 catalyst (25). When acetonitrile was used as a solvent, $Cu_2(OH)PO_4$ catalyst showed phenol conversion of 8.9%. Interestingly, a change from organic solvents to water led to a significant increase in phenol conversion (28.3%), indicating that water was the best solvent over $Cu_2(OH)PO_4$ catalyst. Water is safe, cheap, and environmentally friendly solvent.

However, the water amount strongly affected phenol conversion and tar selectivity (Table 4). When the amount of water was in the range of 2.5–15 ml, the phenol conversion changed slightly with water amount. When the water amount was above 15 ml, phenol conversion decreased gradually. Additionally, in the range of 2.5–30 ml, the tar selectivity decreased with increasing water amount. Therefore, the optimum solvent amount was 15 ml of water.

Influence of reaction temperature. The activities and product selectivities in the temperature range of 60–90°C for phenol hydroxylation over $Cu_2(OH)PO_4$ catalyst are presented in Table 5. Obviously, both phenol conversion and H_2O_2 efficiency increased with temperature over 60–80°C, and when the temperature was above 80°C they were reduced remarkably. At 60°C, phenol conversion was 17.9% and H_2O_2 efficiency 56.2%, respectively. When the temperature was increased to 80°C, phenol conversion and H_2O_2 efficiency gave 28.3 and 84.6%, respectively.

TABLE 5

Catalytic Activities and Selectivity in Phenol Hydroxylation by H_2O_2 over $Cu_2(OH)PO_4$ Catalyst with Various Reaction Temperatures[a]

Reaction temp. (°C)	Phenol conv. (%)	H_2O_2 eff. (%)	Product selectivities (%)			Tar selectivity[b] (%)
			BQ	CAT	HQ	
60	17.9	56.2	4.4	49.8	45.8	12.8
70	21.4	65.2	1.5	51.0	47.5	16.5
80	28.3	84.6	1.1	52.2	46.7	19.1
90	28.7	86.2	0.6	52.5	46.9	27.9

[a] Other reaction conditions are the same as those in Table 2.

[b] Tar selectivity specified in Ref. (26).

Benzoquinone selectivity decreased with temperature increasing in the range 60–90°C. At 60°C benzoquinone selectivity was 4.4%, and it decreased to 0.6% at 90°C. Higher selectivity for BQ was found at lower temperatures. In contrast, the tar selectivity increased with temperature in the range 60–90°C. At 60°C the tar selectivity was 12.8%, and it increased to 27.9% at 90°C. Higher selectivity for tar was found at higher temperatures. These phenomena were interpreted as showing that the tar was formed by overoxidation of BQ. The tar formation was enhanced when the temperature was increased because side reaction of benzoquinone oxidation to tar proceeded more rapidly at higher temperatures. Similar results were also observed on TS-1 catalyst (27).

Influence of reaction time. The activities and product selectivities in phenol hydroxylation by H_2O_2 for various reaction times over $Cu_2(OH)PO_4$ catalyst are presented in Table 6. Notably, a relatively short reaction time resulted in incomplete conversion of phenol as well as undesirable product selectivity, and the conversion increased with reaction time in the region of 0–4 h. When the reaction time was 0.5 h, phenol conversion was 13.2% and BQ selectivity 8.6%. When the reaction time was 4 h, the conversion was 28.3%. When the reaction time was 8 h, the conversion did not change and was 28.5%, but a great amount of tar was obtained. Suitably long reaction time was beneficial for the conversion of phenol, but it deep oxidation of HQ into BQ and of BQ into tar could not be avoided after longer times. Therefore, the reaction time of 4 h was suitable for phenol hydroxylation over $Cu_2(OH)PO_4$ catalyst.

Influence of catalyst crystal size. The dependence of catalytic activities of the catalysts with various crystal sizes on reaction time is shown in Fig. 3. Notably, the catalyst with smaller size exhibited higher catalytic activity at shorter reaction times. For example, if the catalyst crystal size was

TABLE 6

Catalytic Activities and Selectivity in Phenol Hydroxylation by H_2O_2 over $Cu_2(OH)PO_4$ Catalyst with Various Reaction Time[a]

Reaction time (h)	Phenol conv. (%)	Product selectivity (%)		
		BQ	CAT	HQ
0.5	13.2	8.6	55.6	35.8
1	16.9	6.3	56.7	37.0
4	28.3	1.1	52.2	46.7
6	28.4	3.8	56.9	39.3
8	28.5	2.4	55.8	41.8

[a] Other reaction conditions are the same as those in Table 2.

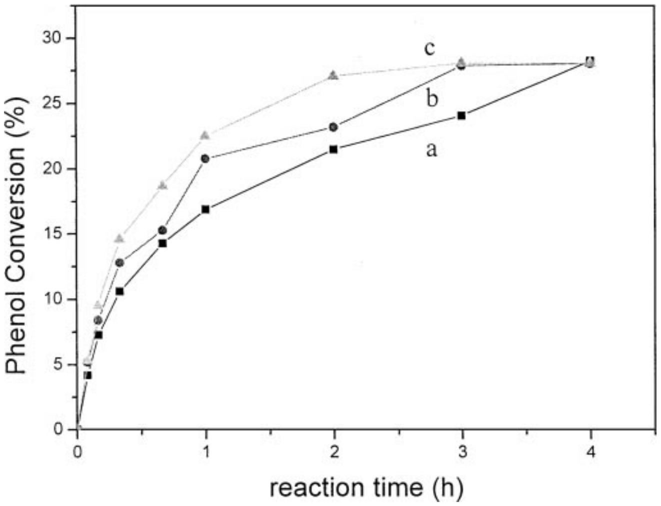

FIG. 3. Activities of the catalysts with various crystal sizes of (a) 150, (b) 15, and (c) 5 μm as a function of reaction time.

5 μm, it exhibited a catalytic activity of 27.6% when the reaction time was 2 h. In contrast, the catalyst with a crystal size of 150 μm showed catalytic activity of 21.2% at the same reaction time (2 h). These results were reasonably assigned to mean that the smaller size provided a larger surface area, and catalytic activity was usually related to exposed active sites (copper species), which increased with surface area.

Influence of catalyst amount. The activities in phenol hydroxylation over $Cu_2(OH)PO_4$ catalyst with different catalyst amount are presented in Table 7. Hydroxylation did not occur in the absence of catalyst. Phenol conversion increased with a catalyst amount of 0–5% (weight ratio of catalyst to phenol). The sample exhibited conversion of 14.6% when the ratio of catalyst to phenol was 1%, and it gave 28.3% conversion when the ratio was 5%. However, when the catalyst amount was larger than 5%, phenol conversion decreased again. For example, when the catalyst amount was 10%, the phenol conversion showed conversion of 16.3%. Addition of a large amount of catalyst to the reaction mixture had a negative effect, which was different from that of TS-1 (22). This is because a larger amount of catalyst hastened the decomposition of H_2O_2. When the catalyst amount was 10%, 9.8% of total H_2O_2 was decomposed, and when the catalyst amount was 5%, 5.6% of H_2O_2 was decomposed. Therefore, a suitable ratio of catalyst to phenol in the catalysis was 5%.

TABLE 7

Catalytic Activities and Selectivity in Phenol Hydroxylation by H_2O_2 over $Cu_2(OH)PO_4$ Catalyst with Various Catalyst Amounts[a]

Catalyst amount (%) (g cat/g phenol)	Phenol conv. (%)	H_2O_2 eff. (%)	Product selectivity (%) BQ	CAT	HQ
0	Inactive	—	—	—	—
1	14.6	46.2	5.4	55.1	39.5
2.5	21.0	65.5	3.8	52.3	43.9
5	28.3	78.0	1.1	52.2	46.7
7.5	19.9	63.4	1.2	51.3	47.5
10	16.3	52.0	1.1	50.9	48.0

[a] Other reaction conditions are the same as those in Table 2.

TABLE 8

Catalytic Activities and Selectivity in Phenol Hydroxylation by H_2O_2 over $Cu_2(OH)PO_4$ Catalyst with Various H_2O_2 Concentration[a]

Phenol : H_2O_2 (molar ratio)	Phenol conv. (%) exp.	theor.	H_2O_2 eff. (%)	Product selectivity (%) BQ	CAT	HQ
3 : 1	28.3	33.3	84.6	1.1	52.2	46.7
2 : 1	31.8	50.0	65.8	3.6	54.8	41.6
1 : 1	48.5	100	49.7	2.5	53.6	43.9
1 : 2	68.4	100	35.0	2.3	52.9	44.8
1 : 3	73.1	100	24.5	0.7	55.3	44.0

[a] Other reaction conditions are the same as those in Table 2.

Influence of molar ratio of phenol to H_2O_2. The influence of the molar ratio of phenol to H_2O_2 in phenol hydroxylation over $Cu_2(OH)PO_4$ catalyst is presented in Table 8. A larger molar ratio of phenol to H_2O_2 in the catalysis led to higher efficiency of utilization for H_2O_2, and the tar selectivity increased with the ratio. When the molar ratio of phenol/H_2O_2 was 3/1, H_2O_2 efficiency was 84.6%. When the molar ratio of phenol/H_2O_2 was 1/3, H_2O_2 efficiency was only 24.5%. At the higher H_2O_2 concentrations, more BQ was oxidized to tar by consumption of H_2O_2. A higher ratio of phenol/H_2O_2 led to higher efficiency of H_2O_2.

Mode of H_2O_2 addition. Since H_2O_2 can react with phenol to form the products HQ, CAT, and BQ, the mode of H_2O_2 addition in the catalysis was an important factor for the H_2O_2 efficiency, which would strongly influence the concentration of H_2O_2 in the catalysis system.

Three different modes of H_2O_2 addition were carried out in this work: (I) addition of all H_2O_2 in one lot at room temperature, followed by heating of the reaction mixture to the reaction temperature (80°C); (II) addition of all required H_2O_2 in one-lot at the reaction temperature; (III) addition of H_2O_2 drop-by-drop in a period of 1 h at the reaction temperature.

The catalytic activity and H_2O_2 efficiency in phenol hydroxylation using various modes of H_2O_2 addition over $Cu_2(OH)PO_4$ catalyst are presented in Table 9. When H_2O_2 was added by mode I, the phenol conversion was low (16.3%), as compared with that of mode II. When H_2O_2 was added slowly by using a syringe pump (mode III), phenol conversion and H_2O_2 efficiency were 28.3% and 84.6%,

TABLE 9

Catalytic Activities and Selectivity in Phenol Hydroxylation by H_2O_2 over $Cu_2(OH)PO_4$ Catalyst with Various Modes of H_2O_2 Addition[a]

Mode of addition	Phenol conv. (%)	H_2O_2 eff. (%)	Product selectivity (%)		
			BQ	CAT	HQ
(I) One-lot at RT	16.3	53.2	8.9	54.2	36.9
(II) One-lot at 80°C	25.0	78.0	4.0	51.3	44.7
(III) Drop by drop at 80°C	28.3	84.6	1.1	52.2	46.7

[a] Other reaction conditions are the same as those in Table 2.

respectively. Meanwhile, BQ concentration was low, 1.1%, and the formation of tar was also controlled at 19%. These results indicated that addition of H_2O_2 was preferable to use of mode III.

Regeneration of the catalyst. The catalytic activity of $Cu_2(OH)PO_4$ catalyst was monitored over three runs of the reaction, and the results are presented in Table 10. After the first run of phenol hydroxylation, the activity of $Cu_2(OH)PO_4$ catalyst reduced sharply from 28.3% (first run) to 13.5% (second run), which was assigned to pollution of tar product on the surface of the catalyst. TG analysis on the used catalyst in oxygen atmosphere exhibited a weight loss of about 25% over 500–650°C, confirming that the catalyst surface was partially covered with tar. However, after calcination at 550°C for 2 h, $Cu_2(OH)PO_4$ catalyst regenerated its catalytic activity at initial level, and its XRD (Fig. 1b) and IR spectra were unchanged. These results indicated that the catalyst was regenerable by calcination at 550°C for 2 h.

ESR Investigation

ESR spectra of H_2O_2 with DMPO at room temperature over various catalysts, CuO, $Cu_4O(PO_4)_2$, $Cu_2(OH)PO_4$, and TS-1, are shown in Fig. 4. Obviously, the samples CuO, $Cu_4O(PO_4)_2$, and $Cu_2(OH)PO_4$ showed similar ESR signals at $a_N = a_H =$ 1.49 mT, which were assigned to the adduct of hydroxyl radical with DMPO (DMPO-OH) (28). In contrast, the ESR spectrum of H_2O_2 on TS-1 with DMPO showed typical signals at $a_N = 1.41$ mT, $\mathrm{a}_{\mathrm{H}}^{\beta} = 1.13$ mT, and $\mathrm{a}_{\mathrm{H}}^{\gamma} = 0.13$ mT, which were assigned to the adduct of hydroperoxyl radical with DMPO (DMPO-O_2^-) (29), in good agreement with the reported mechanism of catalytic phenol hydroxylation (23). Notably, the intensity of hydroxyl radicals on various catalysts was obviously distinguishable. On the $Cu_2(OH)PO_4$ catalyst the signals were very strong, while on the CuO catalyst the signals were much weaker. Comparing of the intensity of hydroxyl radicals with catalytic activity on various catalysts, it was very interesting to note that the catalytic conversion increased with the intensity of hydroxyl radicals, as shown in Fig. 5. These results suggested that hydroxyl radicals were important intermediates, which could be responsible for the high activity in the catalysis.

TABLE 10

Catalytic Activities and Selectivity in Phenol Hydroxylation by H_2O_2 over $Cu_2(OH)PO_4$ Catalyst with Regeneration of the Catalyst[a]

Run	Phenol conv. (%)	Product selectivity (%)		
		BQ	CAT	HQ
First run	28.3	1.1	52.2	46.7
Second run (used sample for run 1)	13.5	3.5	53.4	43.1
Third run (regeneration by calcination at 550°C for run 2)	27.2	2.1	52.1	45.8

[a] Other reaction conditions are the same as those in Table 2.

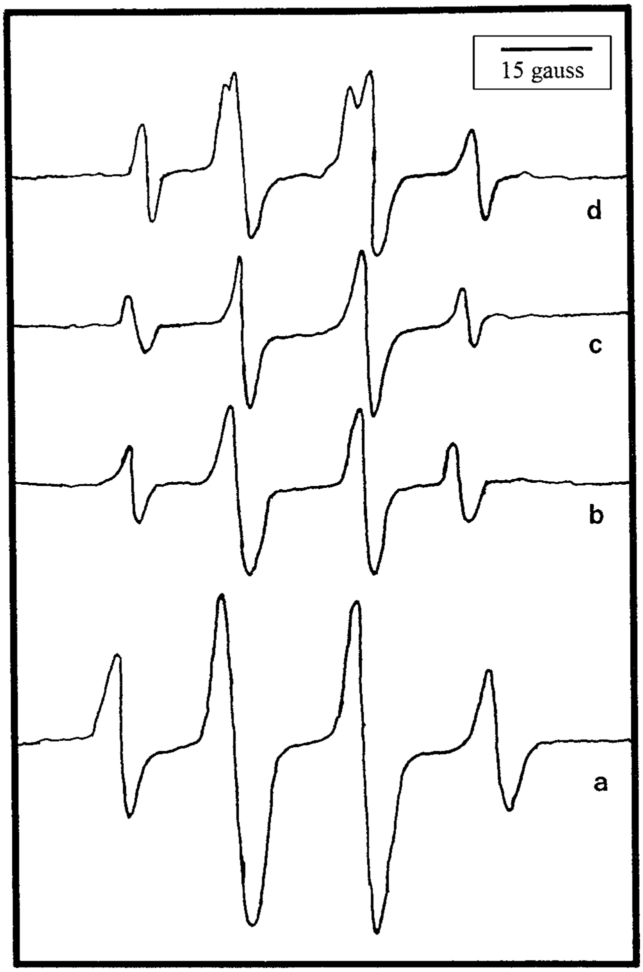

FIG. 4. ESR spectra of H_2O_2 with DMPO over the samples of (a) CuO, (b) $Cu_4O(PO_4)_2$, (c) $Cu_2(OH)PO_4$, and (d) TS-1.

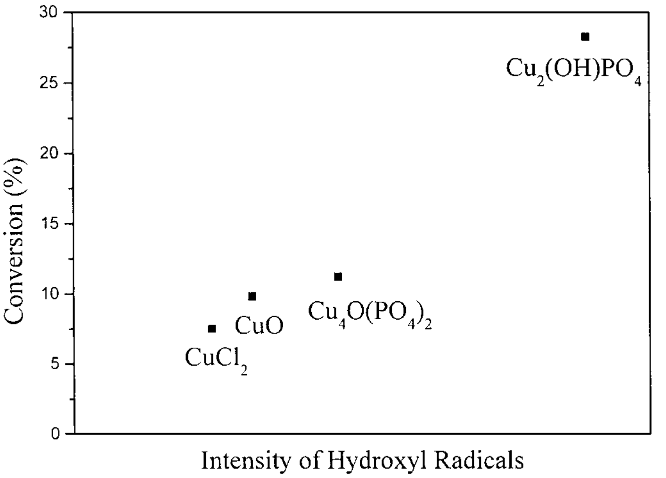

FIG. 5. Dependence of intensity of signals at $a_N = a_H = 1.49$ mT in ESR spectroscopy on the catalytic activity in phenol hydroxylation over various Cu-based catalysts.

After addition of phenol into the reaction mixture of H_2O_2 with DMPO over $Cu_2(OH)PO_4$ catalyst, the characteristic ESR signals assigned to hydroxyl radicals disappeared completely, and the analysis of reaction solution by mass spectroscopy showed typical peaks assigned to diphenols, indicating that the phenol molecules reacted with hydroxyl radicals to form the products of diphenols in phenol hydroxylation by H_2O_2.

The catalytic mechanism in phenol hydroxylation on $Cu_2(OH)PO_4$ catalyst is proposed in Fig. 6. In this mechanism, when Cu^{2+}-OH species react with H_2O_2, the five-ring copper intermediate complex could be formed (30), and a similar model had been reported in the literature (31). Furthermore, the five-ring copper complex gave a catalytically active intermediate of hydroxyl radical. Possibly, OH species in $Cu_2(OH)PO_4$ catalyst could promote production of hydroxyl radicals ($\cdot$OH), which resulted in increased catalytic conversion of phenol hydroxylation.

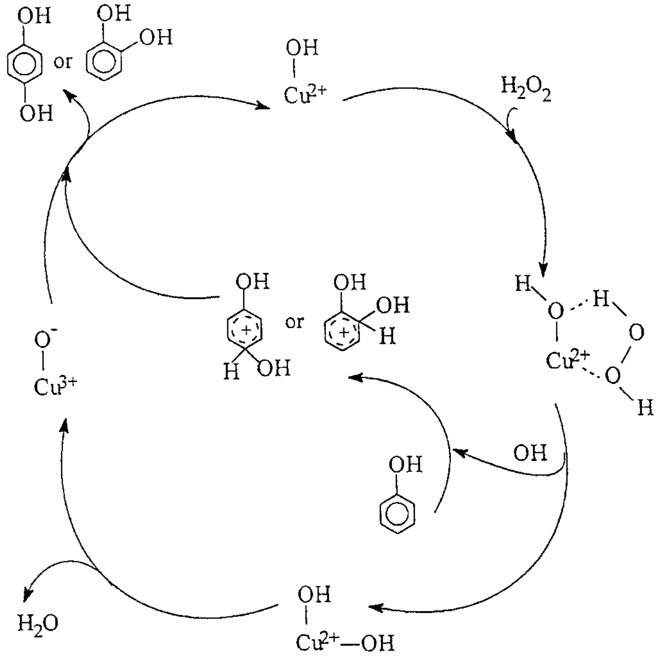

FIG. 6. Proposed mechanism in phenol hydroxylation by H_2O_2 over $Cu_2(OH)PO_4$ catalyst.

Experimentally, both Cu^{2+} and Cu^{3+} were found by cyclic voltammetry in phenol hydroxylation by H_2O_2 over $Cu_2(OH)PO_4$ catalyst (32). Similarly, Cu^{2+}/Cu^{3+} were observed in phenol hydroxylation by H_2O_2 on $La_{2-x}Sr_xCuO_{4\pm\lambda}$ oxide (20). These experimental data were good in agreement with the proposed mechanism.

CONCLUSIONS

A novel catalyst of $Cu_2(OH)PO_4$ was hydrothermally synthesized, and its catalytic data showed that the $Cu_2(OH)PO_4$ catalyst was very active for phenol hydroxylation by H_2O_2, which was comparable to that of TS-1 which was considered the best catalyst for this reaction. ESR spectrum of H_2O_2 with DMPO over $Cu_2(OH)PO_4$ catalyst showed typical signals assigned to hydroxyl radicals, the intensity of which was proportional to the catalytic activity. These results suggested that hydroxyl radicals were major active intermediates, which could be responsible for the high activity in phenol hydroxylation over $Cu_2(OH)PO_4$ catalyst.

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