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Synthesis of $Cu_2(OH)PO_4$ Crystals with Various Morphologies and Their Catalytic Activity in Hydroxylation of Phenol

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Copper hydroxyphosphate ($Cu_2(OH)PO_4$) crystals with various morphologies have been successfully synthesized by a simple hydrothermal method, using different organic amines as the morphology-controlling agents. These $Cu_2(OH)PO_4$ crystals were used as catalysts for phenol hydroxylation by H_2O_2, and they showed distinct activities. The sheet morphology of $Cu_2(OH)PO_4$ crystals with a large percentage of reactive facets ({011} facets) exhibited enhanced catalytic activity in hydroxylation of phenol.

Copper hydroxyphosphate ($Cu_2(OH)PO_4$), which has been synthesized by hydrothermal synthesis,[1] was discovered in 1823.[2] It has been extensively studied because of its catalytic,[1,3] magnetic,[4] and optical properties.[5] These excellent properties may have a relationship with its special crystal structure.[1,3,6] $Cu_2(OH)PO_4$ has an orthorhombic crystal structure with cell parameters of $a = 8.062$, $b = 8.384$, and $c = 5.881$ Å, and it consists of a PO_4 tetrahedron, a $Cu(1)O_6$ octahedron, a $Cu(2)O_5$ trigonal bipyramid, and an OH group between the two Cu species, in which oxygen atoms are shared with each other.[6] In particular, novel catalytic properties of $Cu_2(OH)PO_4$ for the hydroxylation of phenol[3b] and epoxidation of styrene[7] have been investigated. These excellent catalytic properties originate from the OH species attached to the Cu sites, which act as adsorption sites on the catalyst surface.[1] It is well accepted that there is a close relationship between the morphology and the properties of inorganic materials:[8] that is, morphologies determine the properties since the crystal shape dictates the interfacial atomic arrangement of the material. Therefore, controlling the shape and morphology of inorganic materials may provide opportunities to explore their novel catalytic activity.

It has been reported that copper hydroxyphosphate crystals with various hierarchical superstructures were synthesized by simply adjusting the pH, and NH_4^+ ions played an important role in the aggregation process.[5b] Herein, various morphologies of $Cu_2(OH)PO_4$ crystals were secured via a simple hydrothermal reaction[1] using different organic amines as the morphology controlling agents. Adding different organic amines with the same mole can change the pH value (Table 1) of the reaction system and generate different organic ammonium ions. Moreover, with organic amine as the morphology-controlling agent, twinned crystals and other complex crystals are not generated. When these various morphologies of $Cu_2(OH)PO_4$ crystals were used as catalysts for phenol hydroxylation by H_2O_2, the results showed different catalytic activity.

Figure 1 shows typical SEM images of $Cu_2(OH)PO_4$ crystals prepared at different temperatures with different

**Table 1.** Summary of the experimental conditions, BET surface areas, and corresponding morphologies of $Cu_2(OH)PO_4$ samples

Sample	pH	Temperature /°C	Reaction time /h	BET /$m^2\,g^{-1}$	Morphology
a	1.5	150	72	0.3551	prismatic
b	1.0	100	72	0.0167	octahedron
c	1.0	150	72	0.0011	rod
d	2.5	150	72	0.0640	sheet
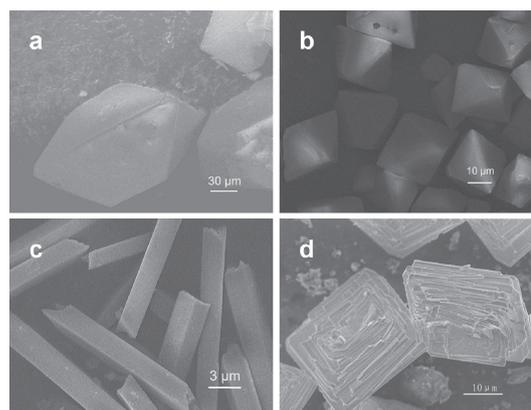
Figure 1. SEM images of various morphologies of $Cu_2(OH)PO_4$ crystals using different morphology-controlling agents: (a) ethylenediamine at 150 °C, (b) tris(hydroxymethyl)aminomethane at 100 °C, (c) tris(hydroxymethyl)aminomethane at 150 °C, and (d) 4,4′-bipyridyl at 150 °C.

morphology-controlling agents in an aqueous solution. There are significant differences in the morphology and crystallite sizes of the $Cu_2(OH)PO_4$ crystals. When the ethylenediamine is added in this hydrothermal process as the morphology-controlling agent (experimental conditions: 1 g of $CuAc_2 \cdot H_2O$, 6.25 mL of H_2O, 1 mL of H_3PO_4 (85 wt %), and 0.35 mL of ethylenediamine at 150 °C for 72 h), the morphology of the as-prepared copper hydroxyphosphate is as shown in Figure 1a, which exhibits a well-defined prismatic crystals. The prism is bounded with four trapezium prism faces and four trigonal end caps. Interestingly, the long rod morphology shown in Figure 1c appeared when we added tris(hydroxymethyl)aminomethane as the morphology-controlling agent into the solution with the same hydrothermal method. At the same time, when we tuned the temperature to 100 °C, the $Cu_2(OH)PO_4$ crystal exhibited octahedron morphology in Figure 1b. Figure 1d showed the sheet morphology obtained when the morphology-controlling agent was changed
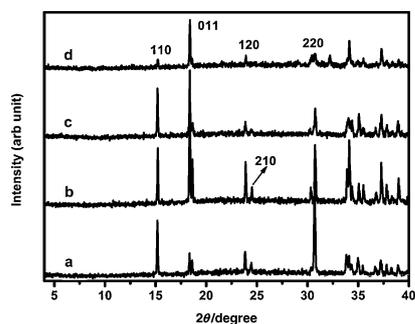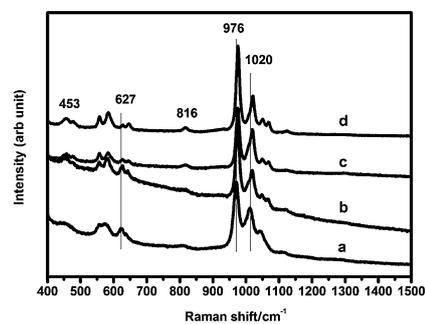
Figure 2. XRD patterns of various morphologies of $Cu_2(OH)PO_4$ crystals using different morphology-controlling agents: (a) ethylenediamine at 150 °C, (b) tris(hydroxymethyl)aminomethane at 100 °C, (c) tris(hydroxymethyl)aminomethane at 150 °C, and (d) 4,4′-bipyridyl at 150 °C.

Figure 3. Raman spectra of various morphologies of $Cu_2(OH)PO_4$ crystals using different morphology-controlling agents: (a) ethylenediamine at 150 °C, (b) tris(hydroxymethyl)aminomethane at 100 °C, (c) tris(hydroxymethyl)aminomethane at 150 °C, and (d) 4,4′-bipyridyl at 150 °C.

Table 2. The calculated cell volumes and lattice parameters of $Cu_2(OH)PO_4$ with various morphologies

Sample	a/Å	b/Å	c/Å	V/Å^3
a	8.074	8.410	5.889	399.89
b	8.060	8.389	5.889	398.19
c	8.045	8.389	5.898	398.04
d	8.060	8.385	5.881	397.43

to 4,4′-bipyridyl with the same hydrothermal method. Based on these SEM results, different organic amines can be the reason for the different morphologies of $Cu_2(OH)PO_4$ crystals. Adding the same number of moles of different organic amines can change the pH value of the reaction system and generate different organic ammonium ions. The surface-adsorbed OH⁻ and all kinds of ammonium ions can lead to linkage by electrostatic attractions and repulsions.[9] It can affect the form of growth units and can then drastically affect the final morphology. Under the condition of addition of tris(hydroxymethyl)-aminomethane, changing the temperature of reaction resulted in different morphologies, but others were not. It was the reason that the pH of tris(hydroxymethyl)aminomethane's buffer solution changed with the temperature. However, the pH exerts an important influence on the synthesis of $Cu_2(OH)PO_4$ crystals with various morphologies.[3b]

The XRD pattern (Figure 2) of as-synthesized copper hydroxyphosphate crystals with different morphologies showed several obvious peaks at 15.2, 18.5, 31.0, 34.2, and 37.3° in the range of 4–40°. Based on above XRD result, we can see that various morphologies of copper hydroxyphosphate crystals the exhibited by the same phase. No diffraction peaks for other phases or materials or copper phosphate hydrate are observed in XRD patterns, indicating a high purity and crystallinity of the final products. However, the relative intensities of the diffraction peaks for one sample are obviously different from those for other samples, which is attributed to the variations in the morphology. For example, higher intensity for the (011) plane as compared with other planes in Figure 2d is attributed to the sheet morphology. According to the XRD analysis, the percentage of (011) plane of $Cu_2(OH)PO_4$ crystals is 4.51% (a), 18.85% (b), 14.42% (c), and 21.97% (d). Therefore, from these XRD results, it is expected that changing the organic amines in this reaction system involves variations of the morphology and crystal structure. Moreover, these variations of the crystal structure, which correspond with a change in the morphology, significantly influenced the catalytic activity in hydroxylation of phenol.

To further understand the variations in crystal structure with morphology, Raman spectra of various morphologies of $Cu_2(OH)PO_4$ crystals were also obtained and are shown in Figure 3. The ν_1 and ν_2 mode of the phosphate vibration were observed at 976 and 453 cm⁻¹, respectively. The Raman bands at 1020 cm⁻¹ was attributed to the ν_3 mode. The ν_4 modes were found at 557, 627, and 646 cm⁻¹. The lattice OH⁻ vibration bands for all the crystals were observed at 816 cm⁻¹. However, we can see that the peaks corresponding to 627, 976, and 1020 cm⁻¹ of Figure 3a were shifted to lower frequencies in comparison with Figure 3b, Figure 3c, and Figure 3d, which provided important information on the variation of the local crystal structure with changes in the morphology. The lower wavenumbers for the Raman stretching bands correspond to the longer P–O bond lengths.[5b,10] That coincided with the cell volume determined by XRD analysis, as shown in Table 2. Therefore, the result of Raman spectra demonstrated that the crystal structure of $Cu_2(OH)PO_4$ changed as the morphology was varied by changing the morphology-controlling agents. The catalytic activity in hydroxylation of phenol will also change with the crystal structure.

Figure 4 shows the electron paramagnetic resonance (EPR) spectroscopy of as-prepared $Cu_2(OH)PO_4$ crystals with different morphologies. As displayed in Figure 4, the g value ($g_a = 2.08$, $g_b = 2.10$, $g_c = 2.13$, $g_d = 2.06$) of each sample is different. That is caused by the asymmetric crystal structures, such as the changes in the P–O bond lengths (shown in Figure 3). The distinctions of signal intensity are attributed to the difference in the long-range dipolar interactions between neighboring Cu(II) sites within $Cu_2(OH)PO_4$ crystals. The above results also indicate the variations of crystal structure and morphology.

As shown in Table 1, various morphologies of $Cu_2(OH)PO_4$ crystals have the small BET surface areas. Therefore, the BET surface areas cannot determine the catalytic activity in hydroxylation of phenol. It has been reported that the $Cu_2(OH)PO_4$ catalyst was very active for phenol hydroxylation by H_2O_2, and hydroxyl radicals were major active intermediates, which could

Figure 4. EPR spectra of various morphologies of $Cu_2(OH)PO_4$ crystals using different morphology-controlling agents: (a) ethylenediamine at 150 °C, (b) tris(hydroxymethyl)aminomethane at 100 °C, (c) tris(hydroxymethyl)aminomethane at 150 °C, and (d) 4,4′-bipyridyl at 150 °C.
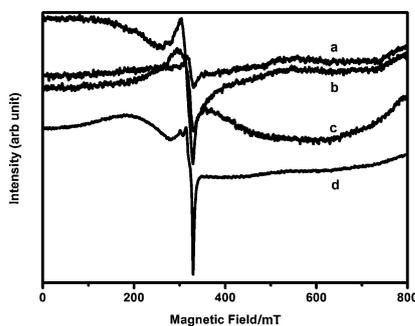
Table 3. Catalytic activities and selectivity in phenol hydroxylation by H_2O_2 over various morphologies of $Cu_2(OH)PO_4$ catalysts using different morphology-controlling agents: (a) ethylenediamine at 150 °C, (b) tris(hydroxymethyl)aminomethane at 100 °C, (c) tris-(hydroxymethyl)aminomethane at 150 °C, and (d) 4,4′-bipyridyl at 150 °C[a]

Catalyst	Phenol conv./%	H_2O_2 eff. conv.[b]/%	Tar yield[d] /%	Product selectivity/%[c]		
				CAT	HQ	BQ
a	20.3	62.3	14.2	72.1	25.4	2.5
b	25.4	77.0	14.1	64.3	34.6	1.1
c	22.3	69.2	13.1	75.7	21.0	3.3
d	30.7	92.6	13.2	57.7	41.7	0.6

[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).[11] [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]The yield of star was as follow: Tar yield = 100 × tar/total phenol added (weight ratio).

be responsible for the high activity in phenol hydroxylation over $Cu_2(OH)PO_4$ catalyst.[1] The catalytic activity of copper hydroxyphosphate crystals with various morphologies were evaluated via the hydroxylation of phenol by H_2O_2. Table 3 shows the catalytic activities and selectivity in phenol hydroxylation by H_2O_2 over $Cu_2(OH)PO_4$ catalysts with various morphologies. The solvent, reaction temperature, reaction time, 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 have been investigated in the previous work.[1] We can see that the $Cu_2(OH)PO_4$ crystals with sheet morphology exhibit the best catalytic activity in hydroxylation of phenol (Phenol conv. 30.67%). In Figure 2d, the percentage of (011) plane is higher than other planes. The phenol conv. (d > b > c > a) in Table 3 corresponds to the percentage of (011) plane (d > b > c > a) in Figure 2. This demonstrates that the {011} facet is the highly reactive facet of $Cu_2(OH)PO_4$ crystal. The previous work suggested that phenol hydroxylation by H_2O_2 over $Cu_2(OH)PO_4$ was a process of radical reactions, and hydroxyl radicals were major active intermediates, which could

be responsible for the high activity in phenol hydroxylation over the $Cu_2(OH)PO_4$ catalyst.[1] Further, the crystal structure of $Cu_2(OH)PO_4$ was responsible for the production rate and quantity of hydroxyl radicals. Therefore, the {011} facet of $Cu_2(OH)PO_4$ crystal can generate more hydroxyl radicals than other facets can. It can be concluded that the $Cu_2(OH)PO_4$ crystals with sheet morphology showed a large percentage of {011} facets. Therefore, we have synthesized the $Cu_2(OH)PO_4$ crystals with a large percentage of reactive facets ({011} facets) using 4,4′-bipyridyl as the morphology-controlling agent, and these crystals exhibit enhanced catalytic activity in hydroxylation of phenol.

In summary, $Cu_2(OH)PO_4$ crystals with various morphologies were synthesized via a simple hydrothermal method[1] using different organic amines as the morphology-controlling agents. By changing the organic amines from ethylenediamine to others, the $Cu_2(OH)PO_4$ crystals showed several morphologies, such as prism, octahedron, long rod, and sheet. As determined by XRD, SEM, Raman spectra, and catalytic activities analyses, the crystal structure of $Cu_2(OH)PO_4$ crystals changed with the variation of the morphology, which led to variations in the catalytic activity in hydroxylation of phenol. The sheet morphology of $Cu_2(OH)PO_4$ crystals with a large percentage of reactive facets ({011} facets) exhibited enhanced catalytic activity in hydroxylation of phenol. This facile hydrothermal process using different organic amines as the morphology-controlling agent may be applied to synthesize other inorganic phosphate materials with controllable structures.

References and Notes
1 F.-S. Xiao, J. Sun, X. Meng, R. Yu, H. Yuan, J. Xu, T. Song, D. Jiang, R. Xu, *J. Catal.* **2001**, *199*, 273.
2 http://www.mindat.org/min-2394.html (Accessed January, 2008).
3 a) X. Meng, K. Lin, X. Yang, Z. Sun, D. Jiang, F.-S. Xiao, *J. Catal.* **2003**, *218*, 460. b) F.-S. Xiao, J. Sun, X. Meng, R. Yu, H. Yuan, D. Jiang, S. Qiu, R. Xu, *Appl. Catal., A* **2001**, *207*, 267. c) X. Meng, Z. Sun, S. Lin, M. Yang, X. Yang, J. Sun, D. Jiang, F.-S. Xiao, S. Chen, *Appl. Catal., A* **2002**, *236*, 17. d) X. Meng, Z. Sun, R. Wang, S. Lin, J. Sun, M. Yang, K. Lin, D. Jiang, F.-S. Xiao, *Catal. Lett.* **2001**, *76*, 105.
4 A. A. Belik, H.-J. Koo, M.-H. Whangbo, N. Tsujii, P. Naumov, E. Takayama-Muromachi, *Inorg. Chem.* **2007**, *46*, 8684.
5 a) S. N. Reddy, R. V. S. S. N. Ravikumar, B. J. Reddy, P. S. Rao, *Ferroelectrics* **1995**, *166*, 55. b) I.-S. Cho, D. W. Kim, S. Lee, C. H. Kwak, S.-T. Bae, J. H. Noh, S. H. Yoon, H. S. Jung, D.-W. Kim, K. S. Hong, *Adv. Funct. Mater.* **2008**, *18*, 2154.
6 A. Cordsen, *Can. Mineral.* **1978**, *16*, 153.
7 X. Meng, K. Lin, J. Sun, M. Yang, D. Jiang, F.-S. Xiao, *Catal. Lett.* **2001**, *71*, 241.
8 a) L. Zhang, W. Wang, L. Zhou, H. Xu, *Small* **2007**, *3*, 1618. b) P. Yang, A. H. Rizvi, B. Messer, B. F. Chmelka, G. M. Whitesides, G. D. Stucky, *Adv. Mater.* **2001**, *13*, 427. c) S. Mann, *Angew. Chem., Int. Ed.* **2000**, *39*, 3392. d) H. Cölfen, M. Antonietti, *Angew. Chem., Int. Ed.* **2005**, *44*, 5576. e) S. Busch, U. Schwarz, R. Kniep, *Adv. Funct. Mater.* **2003**, *13*, 189.
9 a) I. M. Arabatzis, P. Falaras, *Nano Lett.* **2003**, *3*, 249. b) W. Bu, Y. Xu, N. Zhang, H. Chen, Z. Hua, J. Shi, *Langmuir* **2007**, *23*, 9002.
10 a) W. J. Ray, Jr., J. W. Burgner, II, H. Deng, R. Callender, *Biochemisty* **1993**, *32*, 12977. b) L. Popović, D. de Waal, J. C. A. Boeyens, *J. Raman Spectrosc.* **2005**, *36*, 2.
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