Catalytic epoxidation of styrene by molecular oxygen over a novel catalyst of copper hydroxyphosphate $Cu_2(OH)PO_4$

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Catalytic epoxidation of styrene by molecular oxygen over a novel copper hydroxyphosphate catalyst, $Cu_2(OH)PO_4$, was studied. Catalytic data show that the catalyst $Cu_2(OH)PO_4$ is very active, and the main products are benzaldehyde and styrene epoxide. Some important factors associated with the catalytic activity and selectivity have been investigated extensively.

KEY WORDS: styrene epoxidation; molecular oxygen; copper hydroxyphosphate

1. Introduction

Epoxides are important intermediates in the organic synthesis of fine chemicals [1,2], and recently titanosilicalite (TS-1) has shown good catalytic activity and selectivity in the epoxidation of styrene with H_2O_2 as oxidant under mild reaction conditions [3,4]. However, the main product of the epoxidation of styrene with H_2O_2 over TS-1 is phenylacetaldehyde, which is isomeric with the epoxide. In order to increase the selectivity for styrene epoxide, many efforts have been made to find new catalysts with good activity and selectivity for this reaction [5–8].

More recently, much attention has been paid to the use of molecular oxygen for oxidation of hydrocarbons in mild conditions because molecular oxygen is much cheaper than hydrogen peroxide [9–11]. For example, Thomas *et al*. reported the oxidation of *n*-alkanes at the terminal carbon atoms with high selectivity using molecular oxygen in a liquid-phase reaction [9]; Sheldon and co-workers reported the oxidation of alcohols to aldehydes and ketones in water solvent reaction [10].

It has been reported that some catalysts have been found very active in styrene epoxidation by molecular oxygen, including chloride [5], $[Ru^{III}(EDTA)(H_2O)]^-$ [12,13] and transition metal porphyrins such as Mn(II, III), Fe(II, III), Co(II), Cu(II) and Ru(II) catalysts [14–18], and in these conditions the catalytic reactions are homogeneous. Generally, homogeneous catalysis is relatively complex for separation of catalysts from products, as compared with heterogeneous catalysis. Therefore, styrene epoxidation by molecular oxygen over heterogeneous catalysts is desirable.

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In a previous study, we have found that a novel copper hydroxyphosphate catalyst, $Cu_2(OH)PO_4$, is very active in catalytic oxidations of aromatics by H_2O_2 [19], and epoxidation of styrene by H_2O_2 shows high catalytic conversion with high selectivity for the epoxide product [8]. In this work we show the catalytic results in epoxidation of styrene by molecular oxygen over the $Cu_2(OH)PO_4$ catalyst.

2. Experimental

The catalyst used in this work was hydrothermally synthesized using $H_2NCH_2CH_2NH_2$, H_3PO_4, and $CuAc_2$ with molar ratio of $1.0H_2NCH_2CH_2NH_2 : 2.9H_3PO_4 : 1.0CuAc_2 : 25H_2O$. Detailed procedures are shown else-where [8]. A $Cu_4O(PO_4)_2$ sample was prepared from calcination of $Cu_2(OH)PO_4$ at 850 °C for 6 h [19].

The samples were characterized using X-ray diffraction (XRD, Rigaku, D/MAX IIIA) and scanning electron micrography (SEM, Hitachi X-650). The surface area was measured by the sample isotherms of nitrogen at the temperature of liquid nitrogen (BET) using a Micromeritics ASAP 2010M.

The epoxidation of styrene was performed in a 50 ml glass reactor under stirring with a magnetic stirrer. In a standard run, 17.4 mmol of styrene, and 90 mg of catalyst were mixed in the reactor and heated to a given temperature. Then oxygen was introduced into the reactor and sealed in the reaction system. After the reaction for 24 h at 353 K, the products were taken out from the system and analyzed by gas chromatography (GC-17A, Shimadzu, using a flame ionization detector) with a flexible quartz capillary column coated with OV-17. The volume of oxygen consumed in catalytic styrene epoxidation was measured with a gas-detection equipment made by ourselves.

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Table 1
Catalytic activities in styrene epoxidation by molecular oxygen over various catalysts.[a]

Catalyst	Styrene conv. (%)	O_2 (mmol)	TOF[b] (h^{-1})	Product selectivity (%)				
				Styrene epoxide	Phenylacetaldehyde	Benzaldehyde	Benzoic acid	Others[c]
Na_3PO_4	–	–	–	–	–	–	–	–
CuO	9.9	2.1		0	0	100	0	0
$CuCl_2$	18.3	3.5		19.8	15.3	52.1	8.2	4.5
$Cu_4O(PO_4)_2$	27.7	5.2		20.0	0	80.0	0	0
$Cu_2(OH)PO_4$	30.2	6.0	167	16.9	14.4	60.1	5.5	3.1
$Cu_2(OH)PO_4$[d]	14.9		658	67.8	0	32.2	0	0
Solution[e]	–	–	–	–	–	–	–	–
$CoCl_2$[f]	30.0			–	–	16.0	41.0	43.0
TS-1	12.6	2.6	0.8	8.3	9.6	55.9	0.4	25.8
TS-1[g]	18.2		9.1	13.3	58.3	29.0	1.4	

[a] Reaction conditions: styrene 17.4 mmol, catalyst 90 mg, time 24 h, temperature 353 K, no solvent.
[b] Moles of styrene converted per mole of Cu on the surface of the catalyst per hour.
[c] Others are mainly phenylacetic acid formed by the oxidation of phenylacetaldehyde and some ether.
[d] Catalytic styrene epoxidation by H_2O_2 reported in [8].
[e] 90 mg of $Cu_2(OH)PO_4$ catalyst was added into 2.5 ml of acetonitrile and stirred for 24 h. Then the catalyst was removed by filtering, and the solution was used as the reaction catalyst. No extra catalyst was added into the solution, and other conditions did not changed.
[f] Catalytic styrene epoxidation by O_2 reported in [5].
[g] Styrene epoxidation by H_2O_2 reported in [4].

3. Results and discussion

Characterization of the N_2 isotherm for the $Cu_2(OH)PO_4$ catalyst exhibits a very low adsorption amount, and the BET surface area is estimated at 1.4 m^2/g only, indicating that there are no micropores or mesopores.

Catalytic activities and selectivities in styrene epoxidation by molecular oxygen at 353 K over various catalysts are presented in table 1. Na_3PO_4 is catalytically inactive. However, a series of copper compounds such as $CuCl_2$, CuO, $Cu_4O(PO_4)_2$, and $Cu_2(OH)PO_4$, are catalytically active, giving conversion in the range of 9.9–30.2%. These results suggest that copper species are catalytically active sites in the catalysis. Additionally, TS-1 is also active when O_2 is used as oxidant, but the activity reduces significantly, as compared with the catalytic result with H_2O_2 [4].

Furthermore, after stirring for 24 h the solution (table 1) does not contain any copper ions, and catalytic results show that the solution is completely inactive as a catalyst for the styrene epoxidation, which suggests that the reaction is really heterogeneous catalysis.

In particular, styrene conversions over the $Cu_2(OH)PO_4$ catalyst prepared from hydrothermal crystallization and the $Cu_4O(PO_4)_2$ catalyst prepared from calcination of $Cu_2(OH)PO_4$ at 850 °C for 6 h are very high, giving 27.7 and 30.2%, respectively. Because the surface area of the $Cu_2(OH)PO_4$ catalyst is small (1.4 m^2/g) and only the sites on the surface can interact with reactants in catalysis, very high turnover frequency (167 h^{-1}) of $Cu_2(OH)PO_4$ is achieved, which is nearly 200 times that of TS-1 (0.8 h^{-1}). The unusual catalytic activities in the epoxidation of styrene over the $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts may be related to the unique structure of the two catalysts. It has been reported that the two catalysts have the same copper species including chemical state and coordination number [19,20]. The structure of $Cu_2(OH)PO_4$ consists of PO_4 tetrahedron, $Cu(1)O_5$ trigonal bipyramid, $Cu(2)O_6$ octahedron, and OH group between two Cu species, in which oxygen atoms are shared each other. In contrast, the structure of $Cu_4O(PO_4)_2$ has PO_4 tetrahedron, $Cu(1)O_5$ trigonal bipyramid, and $Cu(2)O_6$ octahedron [20].

Obviously, catalytic selectivities over $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts are different. $Cu_4O(PO_4)_2$ gives epoxide and benzaldehyde only, and benzaldehyde selectivity is 80%. In contrast, $Cu_2(OH)PO_4$ shows epoxide, phenylacetaldehyde, benzaldehyde, and benzoic acid. Notably, the difference in structure between $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ is only the OH species attached to Cu sites [19,20]. Therefore, we suggest that the OH species attached to Cu sites play an important role for the product selectivity in the catalysis.

Furthermore, the selectivity of the epoxide and benzaldehyde in the styrene epoxidation by molecular oxygen over $Cu_2(OH)PO_4$ changes greatly, as compared with that by H_2O_2 [8]. In the case of H_2O_2, styrene epoxide is the main product, benzaldehyde is only 32.2%, and no phenylacetaldehyde is detected. When molecular oxygen is used as oxidant, benzaldehyde is the main product (60.1%), epoxide reduces greatly (16.9%), and some phenylacetaldehyde (14.4%) and benzoic acid (5.5%) are detected. These results are reasonably assigned to different reaction routes, as proposed in figure 1. In the case of H_2O_2, isomerization of epoxide hardly occurs (reaction route I) in epoxidation of styrene [8]. When O_2 was used as oxidant, the isomerization of epoxide could take place after the reaction for a long time.

Figure 2(a) shows the dependence of catalytic conversion on reaction time in styrene epoxidation by O_2 over the $Cu_2(OH)PO_4$ catalyst. At the beginning of the reaction (0–4 h) the conversion of styrene is very low, and the product is mostly benzaldehyde; during 4–24 h the conversion increases with reaction time; after a reaction time of 32 h,

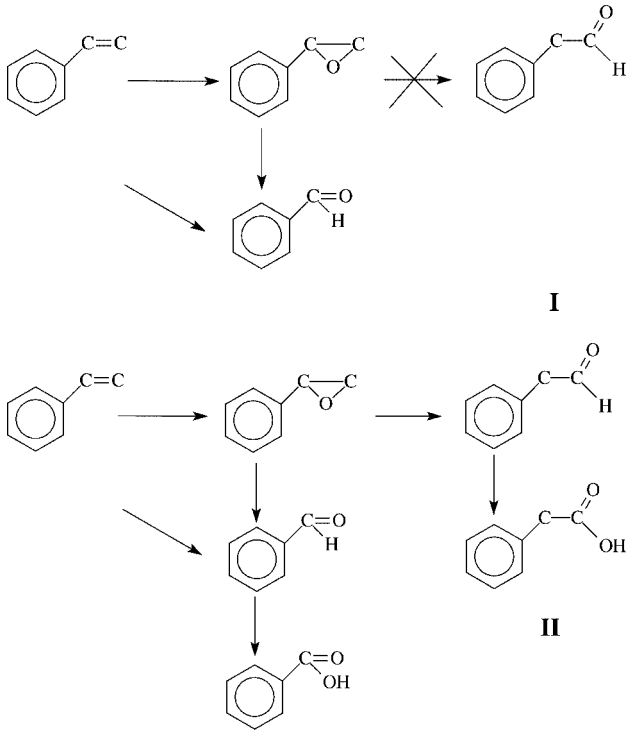

Figure 1. Proposed reaction routes in styrene epoxidation by H_2O_2 (**I**) or by molecular oxygen (**II**) over $Cu_2(OH)PO_4$ catalysts.

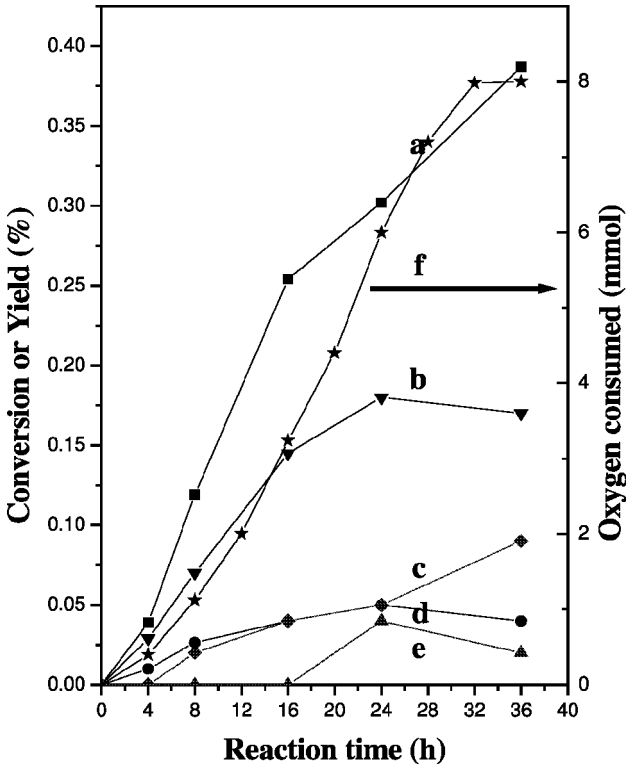

Figure 2. (a) Styrene conversion in styrene epoxidation by molecular oxygen over the $Cu_2(OH)PO_4$ catalyst; the product yields of (b) benzaldehyde, (c) benzoic acid, (d) styrene epoxide, and (e) phenylacetaldehyde in styrene epoxidation by molecular oxygen over $Cu_2(OH)PO_4$; (f) the amount of O_2 consumed in styrene epoxidation by molecular oxygen over $Cu_2(OH)PO_4$ as a function of reaction time. (Reaction temperature is 353 K, and no solvent in the reaction.)

the reaction conversion turns slow. This is interpreted by the destruction of the catalyst structure due to the interaction of the catalyst with a large amount of benzoic acid and phenylacetic acid formed in the reaction (figure 2(c)). The destruction of the catalyst after a reaction time of 32 h is also confirmed by the color changing into green at that time.

The dependence of product selectivity on reaction time in styrene epoxidation by molecular oxygen over $Cu_2(OH)PO_4$ is shown in figure 2 (b)–(e). Benzaldehyde (curve (b)) is the major product, while benzoic acid (curve (c)), styrene epoxide (curve (d)) and phenylacetaldehyde (curve (e)) are relatively low. The yield of benzaldehyde (curve (b)) and styrene epoxide (curve (d)) increases with the reaction time (0–24 h), and then decreases slightly due to the oxidation of benzaldehyde into benzoic acid and isomerization of styrene epoxide into phenylacetaldehyde, respectively. Benzoic acid (curve (c)) is not formed at the beginning of the reaction (0–4 h), but then it forms and increases with the reaction time up to the end of the reaction. The yield of phenylacetaldehyde (curve (e)) is low as compared with the other products in the reaction. The phenylacetaldehyde is formed at a reaction time of 16 h, and after 24 h it decreases with reaction time due to the isomerization into phenylacetic acid.

The dependence of the amount of molecular oxygen consumed on reaction time in styrene epoxidation by molecular oxygen over the $Cu_2(OH)PO_4$ catalyst is shown in figure 2(f). At the beginning of the reaction (0–4 h) only a little benzaldehyde and styrene oxide are formed, and a small amount of O_2 is consumed in the reaction. During reaction time of 4–24 h, with the formation of benzaldehyde, styrene oxide, and benzoic acid, the amount of O_2 consumed in the reaction increases remarkably. After 32 h reaction time, the amount of O_2 consumed in the reaction basically remains unchanged, indicating that the catalytic oxidation is almost finished due to the destruction of the $Cu_2(OH)PO_4$ catalyst.

Table 2 presents the dependence of catalytic activity and selectivity on various amounts of acetonitrile solvent in styrene epoxidation by molecular oxygen over $Cu_2(OH)PO_4$ catalyst. Obviously, the catalytic conversion of styrene decreases with the solvent amount (0–7.5 ml), while the selectivity for styrene epoxide remarkable increases.

The effect of reaction temperature in styrene epoxidation by molecular oxygen over $Cu_2(OH)PO_4$ catalyst is presented in table 3. When the temperature is increased from 333 to 353 K, the conversion increases with the temperature from 9.0 to 30.2%. When the temperature is at 353–363 K, the conversion decreases with the temperature, and at 363 K the conversion is only 25.2%. The higher temperature (363 K) in the reaction gives higher selectivity for benzoic acid, which may destroy the structure of the $Cu_2(OH)PO_4$ catalyst in shorter reaction time (24 h), leading to the decrease of styrene conversion at 363 K. Interestingly, at the temperature 333 K $Cu_2(OH)PO_4$ exhibits only benzaldehyde as product, and at the temperature 343–363 K $Cu_2(OH)PO_4$ shows the products benzaldehyde, styrene epoxide, benzoic acid, and others.

Table 2
Effect of solvent amount of acetonitrile in styrene epoxidation by O_2 over the $Cu_2(OH)PO_4$ catalyst.[a]

Solvent amount of acetonitrile (ml)	Styrene conv. (%)	O_2 (mmol)	TOF[b] (h^{-1})	Product selectivity (%)				
				Styrene epoxide	Phenylacetaldehyde	Benzaldehyde	Benzoic acid	Others[c]
0	30.2	6.0	167	16.9	14.4	60.1	5.5	3.1
2.5	19.1	3.9	111	20.1	2.5	67.1	0	0.3
5.0	7.2	1.3	42.0	31.5	0	68.4	0	0.1
7.5	3.1	0.5	17.1	35.2	0	65.8	0	0

[a] Reaction conditions: styrene 17.4 mmol, catalyst 90 mg, time 24 h, temperature 353 K.
[b] Moles of styrene converted per mole of Cu on the surface of the catalyst per hour.
[c] Others are mainly phenylacetic acid formed by the oxidation of phenylacetaldehyde and some ether.

Table 3
Effect of reaction temperature in styrene epoxidation by O_2 over the $Cu_2(OH)PO_4$ catalyst.[a]

Temp. (K)	Styrene conv. (%)	O_2 (mmol)	TOF[b] (h^{-1})	Product selectivity (%)				
				Styrene epoxide	Phenylacetaldehyde	Benzaldehyde	Benzoic acid	Others[c]
333	9.0	1.8	49.8	0	0	100	0	0
343	11.1	2.1	61.4	27.8	3.3	68.8	0	0.1
353	30.2	6	167	16.9	14.4	60.1	5.5	3.1
363	25.2	5.3	139	13.1	7.2	53.2	19.3	8.2

[a] Reaction conditions: styrene 17.4 mmol, catalyst 90 mg, time 24 h, no solvent.
[b] Moles of styrene converted per mole of Cu on the surface of the catalyst per hour.
[c] Others are mainly phenylacetic acid formed by the oxidation of phenylacetaldehyde and some ether.

Table 4
Effect of solvents in epoxidation of styrene by O_2 over the $Cu_2(OH)PO_4$ catalyst.[a]

Solvent	Styrene conv. (%)	O_2 (mmol)	TOF[b] (h^{-1})	Product selectivity (%)				
				Styrene epoxide	Phenylacetaldehyde	Benzaldehyde	Benzoic acid	Others[c]
Acetonitrile	9.0	1.8	49.8	0	0	100	0	0
Acetone	9.7	1.9	53.7	0	0	100	0	0
Methanol	–	–	–	–	–	–	–	–

[a] Reaction conditions: styrene 17.4 mmol, catalyst 90 mg, time 24 h, temperature 333 K, solvent 2.5 ml.
[b] Moles of styrene converted per mole of Cu on the surface of the catalyst per hour.
[c] Others are mainly phenylacetic acid formed by the oxidation of phenylacetaldehyde and some ether.

The other solvents are also investigated in styrene epoxidation by molecular oxygen over $Cu_2(OH)PO_4$, as presented in table 4. Notably, the catalytic performances in the solvents acetonitrile and acetone are similar, and the styrene epoxidation is completely inactive in the solvent methanol.

4. Conclusion

Copper hydroxyphospate $Cu_2(OH)PO_4$ is an active catalyst in the epoxidation of styrene with molecular oxygen.

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