Catalytic epoxidation of styrene over copper hydroxyphosphate $Cu_2(OH)PO_4$

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Catalytic epoxidation of styrene with hydrogen peroxide over copper hydroxyphosphate $Cu_2(OH)PO_4$ was studied. Catalytic data shows that the catalyst $Cu_2(OH)PO_4$ is very active, and the main products are styrene epoxide and benzaldehyde, particlularly giving high selectivity for styrene epoxide. In contrast, over TS-1 a large amount of phenylacetaldehyde product is formed. Some important factors associated with the catalytic activity and selectivity are investigated extensively.

KEY WORDS: styrene epoxidation; hydrogen peroxide; copper hydroxyphosphate

1. Introduction

Epoxides are important intermediates in organic synthesis of fine chemicals. The direct epoxidation of alkenes generally uses peracids, and the procedures are very costly and usually produce huge amounts of pollutants [1,2]. It is highly desirable to replace the conventional process with an environmentally benign procedure.

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 over TS-1 is phenylacetaldehyde, which is isomeric with the epoxide. Additionally, the small pore size, somewhat complicated synthesis and expensive preparation price will limit its popular application. 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 [5–7]. For example, Li et al. have reported that a Ti–SiO_2 catalyst has high selectivity for styrene epoxide, while the conversion of the styrene is relatively low as compared with that of TS-1 [7].

Recently, we have reported a novel catalyst, copper hydroxyphosphate $Cu_2(OH)PO_4$, which is very active in hydroxylation of aromatics with H_2O_2 [8]. Here we show the catalytic results in epoxidation of styrene by H_2O_2 over copper hydroxyphosphate $Cu_2(OH)PO_4$.

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 1.0 $H_2NCH_2CH_2NH_2$: 2.9 H_3PO_4 : 1.0 $CuAc_2$: 25 H_2O according to the literature procedure. At first, $CuAc_2$ was added into water with stirring for 30 min followed by addition of H_3PO_4. After stirring for 1.5 h, $H_2NCH_2CH_2NH_2$ was added into the mixture, which then was stirred until it became homogeneous. Finally, the gel was sealed in a Telfon-lined stainless-steel autoclave and heated in an oven for 3 days at 140–170 °C. The crystalline product was filtered, washed with distilled water and dried at ambient temperature. A final deep green product with very controlled crystal size (50–500 μm) was obtained. The samples in this work 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 liguid nitrogen (BET) using a Micromeritics ASAP 2010M.

A $Cu_4O(PO_4)_2$ sample was prepared from calcination of $Cu_2(OH)PO_4$ at 850 °C for 6 h [9].

The epoxidation of styrene was performed in a 50 ml glass reactor and stirred with a magnetic stirrer. In a standard run, 17.4 mmol of styrene, 10 ml of acetone as solvent, and 90 mg of catalyst were mixed in the reactor and heated to a given temperature. Then 5.8 mmol of dilute hydrogen peroxide was added into the reactor. After the reaction for 3 h at 318 K, the products were taken out of 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.

3. Results and discussion

N_2 isotherm over $Cu_2(OH)PO_4$ catalyst exhibits 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.

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Table 1
Effect of reaction temperature in epoxidation of styrene with H_2O_2 over copper hydroxyphosphate ($Cu_2(OH)PO_4$).[a]

Catalyst	Styrene conv. (mol%, theoretical)	TOF[b] (h^{-1})	Product selectivity (%)			
			Styrene epoxide	Phenylacetaldehyde	Benzaldehyde	Others[c]
Na_3PO_4	Inactive	–	–	–	–	–
CuO	1.32	0.023	8.15	0	91.9	0
$CuCl_2$	3.42	0.11	7.17	0	70.5	22.3
$Cu_4O(PO_4)_2$	40.5	599	31.3	19.7	35.7	13.3
$Cu_2(OH)PO_4$	44.6	658	67.8	0	32.2	0
TS-1[d]	54.6	9.1	13.3	58.3	29.0	1.4

[a] Styrene/H_2O_2 = 3 (molar ratio), time 3 h, temperature 318 K, 10 ml acetone as solvent.
[b] Moles of styrene converted per mole of Cu on the surface of the catalyst per hour.
[c] Others are mainly benzoic acid formed by the oxidation of benzaldehyde.
[d] From [4].

Catalytic activities and selectivities in styrene epoxidation by H_2O_2 at 318 K over various catalysts are presented in table 1. Na_3PO_4 is catalytically inactive. However, a series of copper compounds such as $CuCl_2$, $CuHPO_4$, CuO, $Cu_2(OH)PO_4$, $Cu_4O(PO_4)_2$, are catalytically active, giving conversion in the range of 1.32–44.6%. These results suggest that copper species are catalytically active sites in the catalysis.

Notably, although the surface area of this novel catalyst is small (1.4 m^2/g) and only the sites on the surface can interact with reactants in catalysis, a very high turnover frequency (658 h^{-1}) of the $Cu_2(OH)PO_4$ is achieved, which is seventy times of that of TS-1 (9.1 h^{-1}).

In particular, styrene conversions on the $Cu_2(OH)PO_4$ catalyst prepared from hydrothermal crystallization and on 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 40.5 and 44.6%, respectively. The unusual catalytic activities in the epoxidation of styrene on 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 [8,9].

Furthermore, catalytic selectivities over $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts are quite different. $Cu_2(OH)PO_4$ gives epoxide and benzaldehyde, and the epoxide selectivity is 67.8%. In contrast, $Cu_4O(PO_4)_2$ shows epoxide, phenylacetaldehyde, and benzaldehyde, and epoxide selectivity is only 31.2%. 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 [8,9]. Therefore, we suggest that the OH species attached to Cu sites play an important role for the product selectivity in the catalysis.

Moreover, catalytic selectivity for products in styrene epoxidation over $Cu_2(OH)PO_4$ and TS-1 catalysts is also different. The $Cu_2(OH)PO_4$ catalyst exhibits very high selectivity for styrene epoxide (67.8%), and there is no phenylacetaldehyde. In contrast, TS-1 shows high yield of phenylacetaldehyde (58.3%) and relatively low selectivity for styrene epoxide. These results are reasonably assigned to different reaction routes, as proposed in figure 1. Over the $Cu_2(OH)PO_4$ catalyst, isomerization of epoxide hardly occurs (reaction route I) in epoxidation of styrene. In contrast, the isomerization of epoxide easily takes place over the TS-1 catalyst.

Figure 2(a) shows the dependence of catalytic conversion in styrene epoxidation on reaction time over $Cu_2(OH)PO_4$. At the beginning of the reaction (0.5 h) the conversion of styrene is very low, and the product is mostly styrene epoxide; during 0.5–3 h the conversion increases significantly; 4 h later, the conversion basically reaches its maximum value.

Dependence of product selectivity on reaction time for the $Cu_2(OH)PO_4$ catalyst is shown in figure 2 (b) and (d). Styrene epoxide (curve (b)) is the major product while benzaldehyde (curve (c)) and phenylacetaldehyde (curve (d)) are relatively minor products. The yields of benzaldehyde (curve (c)) and styrene epoxide (curve (b)) increase with the reaction time before 3 h, and then decrease slightly due to the oxidation of benzaldehyde into benzoic acid and isomerization of styrene epoxide into phenylacetaldehyde, respectively.

The effect of reaction temperature for epoxidation of styrene over $Cu_2(OH)PO_4$ is presented in table 2. When the temperature is increased from 303 to 333 K, the conversion increases slightly from 40.2 to 49.7%, and the selectivity for styrene epoxide decreases greatly from 71.1 to 28.1%. These results are explained by styrene epoxide being transformed into benzaldehyde and benzoic acid by increasing temperature. It seems that benzaldehyde is favorably formed at high temperature, because high temperature will supply high energy to break the C=C bond. At low temperature the energy supplied by the reaction system is not enough to break the C=C bond and formation of styrene epoxide is favored, which is in agreement with the results published in [4,7].

The concentration of H_2O_2 in the reaction system strongly influences the conversion and the selectivity, and there are two ways to change the concentration of H_2O_2: (1) the change in solvent amount or (2) the change in the amount of H_2O_2 added into the reaction mixture. Table 3 presents the dependence of catalytic activity and selectivity on various concentrations of H_2O_2 over $Cu_2(OH)PO_4$. When the solvent amount is 2.5–10 ml, the conversion of styrene changes little, but the selectivities for styrene epoxide, benzaldehyde and benzoic acid change greatly. The product selectivity for

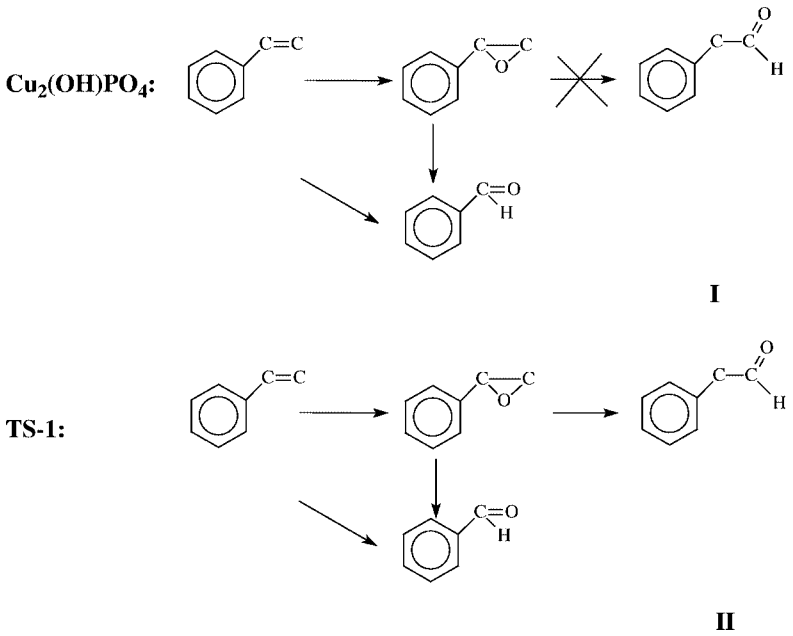

Figure 1. Proposed reaction routes in styrene epoxidation by H_2O_2 over $Cu_2(OH)PO_4$ and TS-1 catalysts.

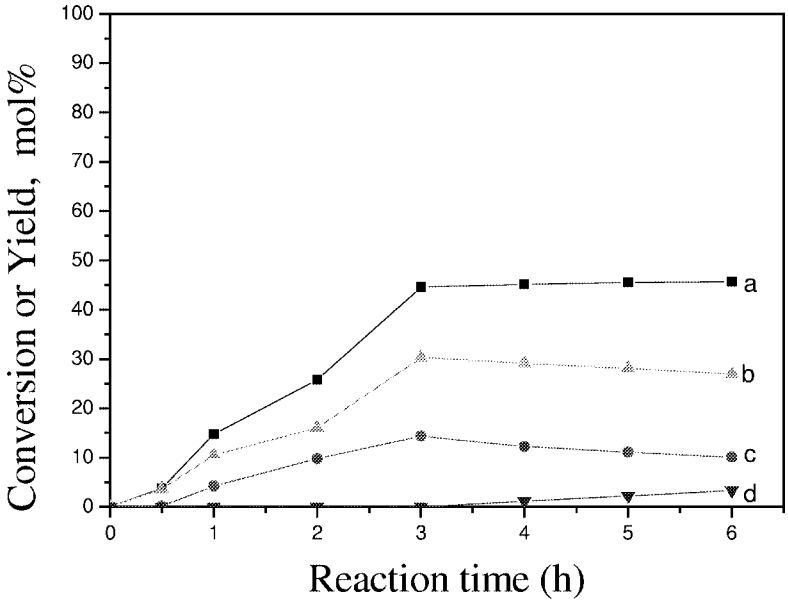

Figure 2. (a) Styrene conversion (mol% of theoretical conversion calculated on the basis of styrene/H_2O_2 molar ratio in the reaction system) and product yields of (b) styrene epoxide, (c) benzaldehyde, (d) phenylacetaldehyde as a function of reaction time. Styrene/H_2O_2 = 3 (molar ratio), reaction temperature 318 K, 10 ml of acetone as solvent.

Table 2
Effect of reaction temperature in epoxidation of styrene with H_2O_2 over copper hydroxyphosphate ($Cu_2(OH)PO_4$).[a]

Temp.	Styrene conv.	TOF[b]	Product selectivity (%)			
	(mol%, theoretical)	(h^{-1})	Styrene epoxide	Phenylacetaldehyde	Benzaldehyde	Others[c]
303	40.2	593	71.1	0	28.9	0
318	44.6	658	67.8	0	32.2	0
333	49.7	733	28.2	0	51.1	20.84

[a] Styrene/H_2O_2 = 3 (molar ratio), time 3 h, 10 ml acetone as solvent.
[b] Moles of styrene converted per mole of Cu on the surface of the catalyst per hour.
[c] Others are mainly benzoic acid formed by the oxidation of benzaldehyde.

Table 3
Effect of concentration of H_2O_2 in epoxidation of styrene with H_2O_2 over copper hydroxyphosphate ($Cu_2(OH)PO_4$).[a]

The amount of solvent (ml)	The molar ratio of styrene to H_2O_2	Styrene conv. (mol%, theoretical)	TOF[b] (h^{-1})	Product selectivity (%)			
				Styrene epoxide	Phenylacetaldehyde	Benzaldehyde	Others[c]
2.5	3	44.1	651	40.4	0	41.3	18.3
5	3	44.5	658	44.8	0	38.9	16.3
7.5	3	43.4	641	58.6	0	35.3	6.1
10	3	44.6	658	67.8	0	32.2	0
15	3	44.4	656	68.1	0	31.9	0
20	3	41.8	618	69.6	0	30.4	0
10	5	67.7	601	75.0	0	25.0	0
10	4	52.1	577	72.3	0	27.0	0
10	2	37.7	836	57.3	3.3	31.3	8.1

[a] Time 3 h, temperature 318 K, acetonile as solvent.
[b] Moles of styrene converted per mole of Cu on the surface of the catalyst per hour.
[c] Others are mainly benzoic acid formed by the oxidation of benzaldehyde.

Table 4
Effect of solvents in epoxidation of styrene with H_2O_2 over copper hydroxyphosphate ($Cu_2(OH)PO_4$).[a]

Solvent	Styrene conv. (mol%, theoretical)	TOF[b] (h^{-1})	Product selectivity (%)			
			Styrene epoxide	Phenylacetaldehyde	Benzaldehyde	Others[c]
Acetonile	33.2	490	51.1	0	48.9	0
Acetone	44.6	658	67.8	0	32.2	0
Methanol	49.7	735	40.2	0	28.4	31.4

[a] Styrene/$H_2O_2 = 3$ (molar ratio), time 3 h, temperature 318 K.
[b] Moles of styrene converted per mole of Cu on the surface of the catalyst per hour.
[c] Others are mainly benzoic acid formed by the oxidation of benzaldehyde.

styrene epoxide increases with solvent amount, while the selectivity for benzaldehyde and benzoic acid decreases with solvent amount during the change in solvent amount of 2.5–10 ml.

When the molar ratio of styrene to H_2O_2 is changed, both the conversion of styrene and the selectivities for products change dramatically. When the ratio of styrene to H_2O_2 is larger (5 : 1), and the amount of H_2O_2 added into the mixture is small, the theoretical molar conversion is higher and the selectivity for styrene epoxide is greater. With the ratio decreasing, both the theoretical conversion and the selectivity for styrene oxide decrease, while the selectivity for benzaldehyde increases. At the same time, some benzoic acid and phenylacetaldehyde are formed.

The other solvents were also used in this reaction and the effects of these solvents over the $Cu_2(OH)PO_4$ catalyst are presented in table 4. Notably, the conversion of styrene and the selectivity for the products in acetonitrile as solvent are like those in acetone, while in methanol solvent another product of ether is formed.

4. Conclusion

Copper hydroxyphosphate $Cu_2(OH)PO_4$ is an active catalyst in the epoxidation of styrene, giving high selectivity for epoxide product, as compared with that over TS-1.

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