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Journal of Catalysis 218 (2003) 460–464

JOURNAL OF
CATALYSIS

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Research Note

Catalytic oxidation of olefins and alcohols by molecular oxygen under air pressure over $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts

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Received 18 November 2002; revised 18 February 2003; accepted 21 February 2003

Abstract

Catalytic oxidation of olefins (styrene and cyclohexene) and alcohols (benzyl alcohol and cyclohexanol) under air pressure by molecular oxygen over $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts has been studied. The catalytic data show that these catalysts are very active in the catalytic oxidation of olefins and alcohols. Adsorption of molecular oxygen on $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts shows a peak at 802 cm^{-1} in infrared (IR) spectroscopy, assigned to adsorbed-oxygen species. Characterization of $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts with molecular oxygen in solvent by electron spin resonance (ESR) spectra shows typical signals assigned to hydroxyl radicals, which may be responsible for the high catalytic activities of the catalysts.

Keywords: Olefin epoxidation; Alcohol oxidation; Infrared spectroscopy (IR); Electron spin resonance (ESR); Peroxide species; Molecular oxygen

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1. Introduction

Selective oxidation of olefins and alcohols to produce epoxides, aldehydes, and ketones is of great importance in the fine chemical and pharmaceutical industries [1–5]. Traditionally, these catalytic procedures produce a great deal of environmentally undesirable wastes because inorganic oxidants and organic solvents are used [5–9]. It is highly desirable to replace the conventional process by an environmentally benign procedure.

Recently, microporous crystals of titanosilicates were discovered which have remarkable catalytic properties for selective oxidation [5,10–14]. For example, TS-1 exhibits high activity and selectivity in the catalytic oxidation of olefins and alcohols using H_2O_2 under mild conditions [13,14]. The use of H_2O_2 is atom efficient and the only by-product is water, which can be designed as green technologies. However, compared with that of molecular oxygen, the relatively high cost of H_2O_2 severely hinders its wide application in catalytic oxidation. Therefore, catalytic oxidation by molecular oxygen would be valuable. Unfortunately, there is no report for pure microporous titanosilicates in the catalytic oxidation of organic substrates by molecular oxygen yet, which is possibly assigned to their almost inactive sites for the activation of molecular oxygen.

There have been a number of successful examples of catalytic oxidation of organic substrates by molecular oxygen, but most research is focused on homogeneous catalysts [15–18]. For example, Sheldon and co-workers report oxidation of alcohols to aldehydes and ketones over homogeneous catalysts of Pd–complex [15b]; Markó and co-workers discovered an efficient, copper-based catalyst that can oxidize a series of alcohols into aldehydes and ketones under mild conditions [17]. More recently, several successful examples of the catalytic oxidation of organic substrates by molecular oxygen over heterogeneous catalysts have been reported [19–22]. Thomas and co-workers show oxidation of n-alkanes at the terminal carbon atoms with high selectivity by using molecular oxygen over microporous aluminophosphates in which Mn or Co species are introduced into the framework as redox centers [19]. Furthermore, Xi and co-workers reported the reaction-controlled phase transfer catalysis for olefin epoxidation by molecular oxygen, which combines the advantages of homogeneous and heterogeneous phases [23]. Notably, although the oxidation of organic substrates by molecular oxygen is carried out under mild conditions, the reaction pressure is still relatively

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doi:10.1016/S0021-9517(03)00079-4

high (near 1 MPa). Therefore, heterogeneous catalysis under much lower pressure such as air pressure is desirable.

Kaneda and co-workers have shown a successful example with high activity and selectivity under air pressure [24]. They synthesized a new Ru–complex heterogeneous catalyst, which gives excellent conversion in aerobic alcohol oxidation. We have reported that copper hydroxyphosphate ($Cu_2(OH)PO_4$) with easy preparation is a good catalyst for catalytic oxidation of organic substrates by H_2O_2 [25–28]. Here, we show the catalytic activity and selectivity in oxidation of olefins (styrene and cyclohexene) and alcohols (benzyl alcohol and cyclohexanol) by molecular oxygen under air pressure over $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts.

2. Experimental

2.1. Preparation of samples

The copper hydroxyphosphate of $Cu_2(OH)PO_4$ was hydrothermally synthesized using $H_2NCH_2CH_2NH_2$, H_3PO_4, and $CuAc_2$ as starting materials with a molar ratio of $1.0H_2NCH_2CH_2NH_2$:$2.9H_3PO_4$:$1.0CuAc_2$:$25H_2O$ [24,28]. First, $CuAc_2$ was mixed with water, followed by the addition of H_3PO_4. After stirring, $H_2NCH_2CH_2NH_2$ was added into the mixture. Then the mixture was stirred until it became homogeneous. Finally, the gel sealed in a steel autoclave was heated in an oven for 3 days at 150 °C. The crystalline product with a crystal size of 50–500 µm was filtered, washed with distilled water, and dried at ambient temperature.

$Cu_4O(PO_4)_2$ was prepared from calcination of $Cu_2(OH)PO_4$ at 850 °C for 6 h [29].

2.2. Characterization of samples

The samples in this study were characterized by X-ray diffraction (XRD), scanning electron micrography (SEM), adsorption of N_2, water, and hexane, differential thermal analysis (DTA), and thermogravimetry analysis (TGA), and infrared spectroscopy (IR).

Infrared spectra of molecular oxygen or organic substrates adsorbed on the samples were recorded on FT-IR spectrometer (PE 430) with resolution of 1 cm^{-1}. Before measurement of molecular oxygen adsorption, the samples were pressed to thin wafers (5 mg/cm^2) and were placed into a quartz cell equipped with KBr windows. The sample disks were evacuated at 400 °C for 2 h (10^{-5} Torr) and cooled to room temperature, then 5 Torr of molecular oxygen or organic substrate was exposed to the disks at room temperature. At the same time, the infrared spectra were recorded. ESR spectra were recorded at room temperature. 5,5-Dimethyl-1-pyrroline *N*-oxide (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 diameter of 1 mm was used. While the reactants were added into the reaction quartz tube, the ESR spectra were measured.

2.3. Catalytic tests

The catalytic tests were performed in a 50-ml glass reactor and stirred with a magnetic stirrer. The substrate and 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 the product was 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 the catalytic test was measured with the gas-detected equipment made by us.

3. Results and discussion

Characterization of $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ crystals shows that both samples are thermally and hydrothermally stable below 650 °C, and the surface area of samples is very small (e.g., surface area of $Cu_2(OH)PO_4$ at 1.4 m^2/g), indicating that there are no micropores or mesopores [25–27].

Table 1 presents catalytic activities and selectivities in styrene by molecular oxygen under air pressure over $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts. Obviously, $CuCl_2$ shows relatively low catalytic activity (18.3%), and the product is only benzaldehyde. However, both $Cu_2(OH)PO_4$ and

Table 1
Catalytic epoxidation of styrene and cyclohexene by molecular oxygen over various samples

Samples	Substrate	Conv.	Product selectivity (%)				
		(%)	P1	P2	P3	P4	P5
$CuCl_2$	Styrene[a]	18.3	0	0	100	0	0
$Cu_2(OH)PO_4$	Styrene[a]	30.2	16.9	14.4	60.1	5.5	3.1
$Cu_4O(PO_4)_2$	Styrene[a]	27.7	20.0	0	80.0	0	0
$Cu_2(OH)PO_4$[b]	Styrene[a]	14.9	67.8	0	32.2	0	0
TS-1[c]	Styrene[a]	18.2	13.3	58.3	29.0	1.4	
$CuCl_2$	Cyclohexene[d]	7.3	3.8	30.2	54.3	11.7	
$Cu_2(OH)PO_4$	Cyclohexene[d]	46.7	4.1	28.5	65.7	1.7	
$Cu_4O(PO_4)_2$	Cyclohexene[d]	45.9	0.3	29.4	68.6	1.7	
$Cu_2(OH)PO_4$[e]	Cyclohexene[d]	28.7	5.0	27.3	38.8	26.7	
TS-1[f]	Cyclohexene[d]	0.5	87	23	0	0	

[a] 17.4 mmol of styrene; 90 mg of catalyst; time, 24 h; temperature, 353 K; no solvent; P1, styrene epoxide; P2, phenylacetaldehyde; P3, benzaldehyde; P4, benzoic acid; P5, phenylacetic acid and some ether.

[b] Molar ratio of styrene: $H_2O_2 = 3$, Ref. [27a].

[c] Molar ratio of styrene: $H_2O_2 = 3$, Ref. [13].

[d] 19.5 mmol of cyclohexene; 81 mg of catalyst; time, 24 h; temperature, 353 K; no solvent; P1, cyclohexene epoxide; P2, cyclohexenol; P3, cyclohexenone; P4, cyclohexanol.

[e] 19.5 mmol of cyclohexene; 81 mg of catalyst; time, 4 h; temperature, 353 K; molar ratio of cyclohexene: $H_2O_2 = 2$; 4 ml acetonitrile as solvent.

[f] Molar ratio of cyclohexene: $H_2O_2 = 2$; Ref. [32].

$Cu_4O(PO_4)_2$ exhibit high catalytic activity by molecular oxygen, giving styrene conversion at 30.2 and 27.7%, respectively, which is comparable to that of homogeneous catalysts of $CoCl_2$ [30] or that of heterogeneous catalysts of TS-1 [13] and $Cu_2(OH)PO_4$ [27a] by use of H_2O_2 oxidant. We also find that over $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts, epoxidation products such as styrene epoxide and phenylacetaldehyde are formed, giving selectivities at 31.3 and 20.0%, respectively.

Notably, in cyclohexene oxidation by molecular oxygen under air pressure, $CuCl_2$ exhibits low conversion (7.3%). However, $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ are very active, giving conversion at 46.7 and 45.6%, and even higher than $Cu_2(OH)PO_4$ by H_2O_2 (28.7%). Additionally, we observe that TS-1 is almost inactive in cyclohexene epoxidation by H_2O_2, which is assigned to the inaccessibility of the small micropores of TS-1 to the large diameter of cyclohexene [31,32]. These results indicate that $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ are potential catalysts for the oxidation of bulky olefins by molecular oxygen.

Table 2 presents catalytic activities and selectivities in the oxidation of benzyl alcohol by molecular oxygen under air pressure over $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts. Obviously, both $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ are catalytically active. For example, $Cu_2(OH)PO_4$ shows conversion at 18.4% with products of benzaldehyde (24.9%), benzoic acid (17.8%), and benzyl benzoate (57.3%) in 24 h; if the reaction time is reduced to 8 h, the conversion of benzyl alcohol decreases to 7.2%, and the selectivity for benzaldehyde and benzoic acid increases to 62.7 and 37.3%, respectively.

Notably, cyclohexanol oxidation shows lower activity than benzyl alcohol oxidation (Table 2). For example, $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ exhibit conversion at 4.8 and 1.9% with only cyclohexanone, as product. Compared with the activity in Table 2, these results suggest that oxidation of primary alcohol is much easier than oxidation of secondary alcohol.

Table 2
Catalytic oxidation of benzyl alcohol and cyclohexanol by molecular oxygen over $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$[a]

Samples	Substrate	Conv. (%)	Product selectivity (%) P1	P2	P3
$Cu_2(OH)PO_4$	Benzyl alcohol[a]	18.4	24.9	17.8	57.3
$Cu_2(OH)PO_4$[b]	Benzyl alcohol[a]	7.2	62.7	32.3	0
$Cu_4O(PO_4)_2$	Benzyl alcohol[a]	9.8	45.3	39.7	15.0
$Cu_2(OH)PO_4$[c]	Benzyl alcohol[a]	24.5	47.9	14.7	37.4
$Cu_2(OH)PO_4$	Cyclohexanol[d]	4.8	100		
$Cu_4O(PO_4)_2$	Cyclohexanol[d]	1.9	100		
$Cu_2(OH)PO_4$[e]	Cyclohexanol[d]	12.1	100		

[a] 21.3 mmol of benzyl alcohol; 104 mg of catalyst; time, 24 h; temperature, 353 K; 2 ml of water as a solvent. P1, benzaldehyde; P2, benzoic acid; P3, benzyl benzoate.

[b] Reaction time, 8 h; other conditions are the same as those in a.

[c] 21.3 mmol of benzyl alcohol; 104 mg of catalyst; time, 6 h; temperature, 353 K; molar ratio of benzyl alcohol, $H_2O_2 = 1$; 2 ml of water as a solvent.

[d] 21 mmol of cyclohexanol, 95 mg of catalyst; time, 24 h; temperature, 353 K; 2 ml of water as a solvent. P1, cyclohexanone.

[e] 21 mmol of cyclohexanol, 95 mg of catalyst; time, 24 h; temperature, 353 K; molar ratio of benzyl alcohol, $H_2O_2 = 1$; 2 ml of water as a solvent.

The question of catalysis leaching in heterogeneous catalysis is very critical. To test the leaching of the catalysts, we performed the following experiments: first, the solvents and the catalysts were mixed and stirred for 24 h. Secondly, the catalysts were filtered and removed, and the reactants were added into the obtained solution. Finally, oxygen was introduced to the reaction system. After reaction for 24 h, no products were detected by GC. These results suggest that these oxidations are truly heterogeneous in nature.

Generally, the catalytic oxidation of alcohols by molecular oxygen is performed under relatively high pressure (0.5–2 MPa). More recently, these alcohols were successfully oxidized by molecular oxygen under air pressure, but the noble transition metals such as Ru–complex are necessary [24]. In this work, we find that copper phosphates with much lower cost are catalytically active for alcohol oxidation by molecular oxygen under air pressure.

The catalytically active species in $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ have been characterized by IR and ESR spectroscopy. As shown in Fig. 1, the adsorption of molecular oxygen on $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts exhibits

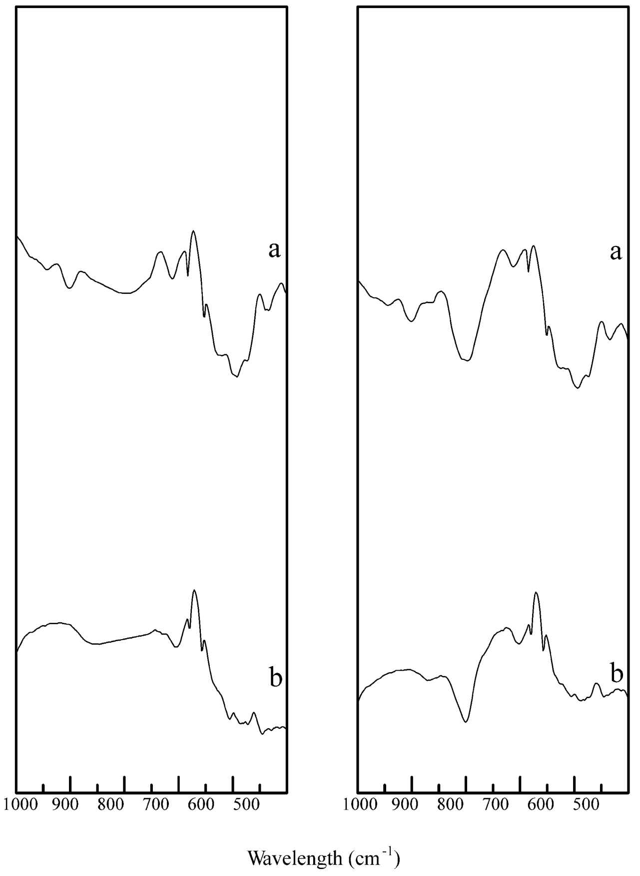


Fig. 1. Left: IR spectra of (a) $Cu_2(OH)PO_4$ and (b) $Cu_4O(PO_4)_2$ samples before adsorption of O_2; right: IR spectra of (a) $Cu_2(OH)PO_4$ and (b) $Cu_4O(PO_4)_2$ samples after adsorption of O_2.

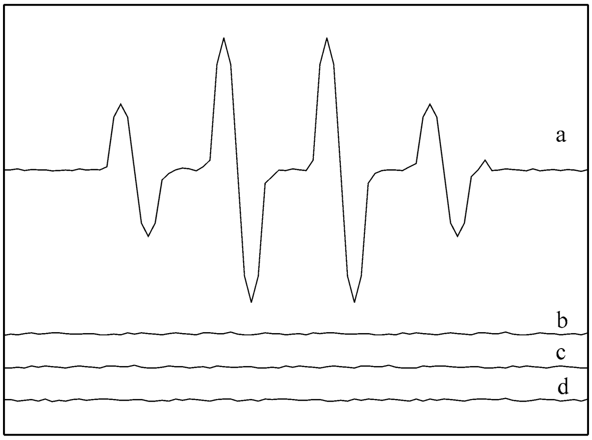


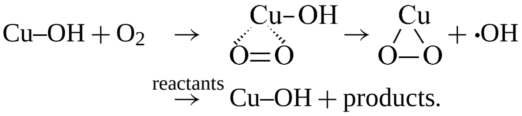
Fig. 2. ESR spectra of (a) $Cu_2(OH)PO_4$, (b) TS-1, (c) CuO, and (d) $CuCl_2$ samples in water after adsorption of O_2 for 24 h.

an obvious band near 802 cm^{-1}, which is stable even if evacuated at room temperature. These results indicate that an interaction of $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts with molecular oxygen can easily occur, forming intermediate-oxygen species.

The assignment of the band near 802 cm^{-1} on $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts is somewhat difficult, but it is comparable to those of published results. Xi et al. have reported that $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3\{PO_4[W(O)_2(O_2)]_4\}$ compound has peroxide species, exhibiting a band at 840 cm^{-1} [23]; Li et al. report that adsorption of molecular oxygen on CeO_2 reduced by H_2 shows peroxide species appearing at 883 cm^{-1} [33]; Jones et al. report that $Mn(TPP)(O_2)$ (TPP, tetraphenylporphyrin) gives peroxide species at 844 cm^{-1} [34]; Urban et al. published that $[Fe^{III}(OEP)O_2]^-$ (OEP, octaethylpophyrinato anion) shows peroxide species at 806 cm^{-1} [35]. Accordingly, the band near 802 cm^{-1} by adsorption of molecular oxygen on $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts may also be assigned to peroxide species, which are possibly active intermediates in the catalytic oxidation of organic substrates by molecular oxygen.

The ESR spectra of various samples in the solvent after adsorption of O_2 are shown in Fig. 2. $Cu_2(OH)PO_4$ catalysts give obvious signals assigned to the adduct of hydroxyl radicals with DMPO (DMPO–OH) [25,36], which is similar to the spectra of $Cu_2(OH)PO_4$ with H_2O_2. After addition of reactants, the signals assigned to radicals disappear completely. These results suggest that the hydroxyl radicals (·OH) may be responsible for the catalytic oxidation of organic substrates. Possibly, formation of the hydroxyl radicals (·OH) in the solution is related to an interaction of $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts with molecular oxygen, which has been confirmed by the appearance of 802 cm^{-1} species in IR spectroscopy, probably assigned to peroxide sites.

Based on all these observations, we propose a tentative mechanism for the formation of peroxide species and hydroxyl radicals as shown in the following scheme:



$$\mathrm{Cu{-}OH} + O_2 \rightarrow \overset{\mathrm{Cu{-}OH}}{\mathrm{O{=}O}} \rightarrow \overset{\mathrm{Cu}}{\mathrm{O{-}O}} + \cdot\mathrm{OH} \xrightarrow{\text{reactants}} \mathrm{Cu{-}OH} + \text{products.}$$

4. Conclusion

$Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ catalysts are catalytically active in the oxidation of olefins (styrene and cyclohexene) and alcohols (benzyl alcohol and cyclohexanol) by molecular oxygen even if under air pressure.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (29825108, 20173022, and 20121103), the State Basic Research Project (G2000077507), and the National Advanced Materials Committee of China. We thank professor Can Li and professor Zuwei Xi of the Dalian Institute of Chemical Physics for helpful suggestion and discussions.

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