Selective Catalytic Oxidation of Diphenol by Metal-Organic Frameworks Cu₃(BTC)₂ Using Hydrogen Peroxide†

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Catalytic oxidation of hydroquinone and pyrocatechol using hydrogen peroxide by metal-organic frameworks of $Cu_3(BTC)_2(H_2O)_3$ with an average size of 1 nm. Significant selectivity was showed in the catalytic oxidation of hydroquinone and pyrocatechol. Also we mainly discussed the influences of reaction temperature and medium to the selectivity by kinetics methods. It was concluded that reaction medium had lager influence on selectivity than temperature.

Keywords: Selectivity, Kinetics, Hydroquinone and pyrocatechol, Metal-organic frameworks.

INTRODUCTION

Metal-organic frameworks (MOFs) compounds with metal oxide/nitride clusters connected by organic linkers show potential applications in catalysis because of their controllable topology geometry and composition. Several authors reported a series of metal-organic frameworks with high chemical stability and high surface area and controllable pore sizes, which present potential applications in catalysis, ion exchange, gas adsorption/separation, sensor technologies, magnetization, luminescence, proton conduction and semiconduction[1-6]. However, the selective catalytic properties of metal-organic frameworks have scarcely been studied, especially by kinetic methods.

In this paper, we selected metal-organic frameworks of $Cu_3(BTC)_2(H_2O)_3$ as catalysts, The selectivity to the oxidation reaction of hydroquinone and pyrocatechol (H_2Q) using hydrogen peroxide was mainly discussed.

EXPERIMENTAL

Frameworks of $Cu_3(BTC)_2(H_2O)_3$ were prepared as described previously[5]. Benzene-1,3,5-tricarboxylate was purchased from Aldrich Chemical Reagent Co., Ltd. Cobalt acetate tetrahydrate, nickearm acetate tetrahydrate, copric nitrate monohydrate, zinc acetate hyexahdrate, hydroquinone, pyrocatechol, hydrochloric acid, and tri-(hydroxymethyl) aminomethane (Tris), alcohol, acetonitrile, were all of analytical grade and purchased from Sinopharm. Double distilled water was used for all kinetic tests. The reaction products were characterized using a Shimadzu UV-3600 UV-visible double-beam scanning spectrophotometer.

RESULTS AND DISCUSSION

Kinetic method of reaction selectivity: Hydroquinone and pyrocatechol were catalyzed by $Cu_3(BTC)_2$ using hydrogen peroxide. A typical UV-visible spectrum shows that successive increase in the absorption maximum of *p*-benzoquinone at 246 nm and decrease in the absorbance of hydroquinone at 289 nm with increasing the reaction time, which is due to the oxidation of hydroquinone to *p*-benzoquinone. As a result, the absorbance A_t was recorded by monitoring the appearance of *p*-benzoquinone at 246 nm *versus* the reaction time t. As shown in Figs. 1 and 2, 274 nm was pyrocatechol's characteristic absorption peak in UV spectra. The characteristic absorption peak presented obvious violet shift and larger absorbance as the reaction time was increased (Figs. 1 and 2). This indicates the formation of *o*-benzoquinone. As a result, the absorbance A_t was recorded by monitoring the appearance of *o*-benzoquinone at 260 nm *versus* the reaction time t. The results revealed that the reaction was of the apparent first order with respect to the H_2Q concentration. After the nonlinear fitting of the experimental data (Fig. 3), a series of the apparent first-order rate constants for oxidation of H_2Q can be calculated.
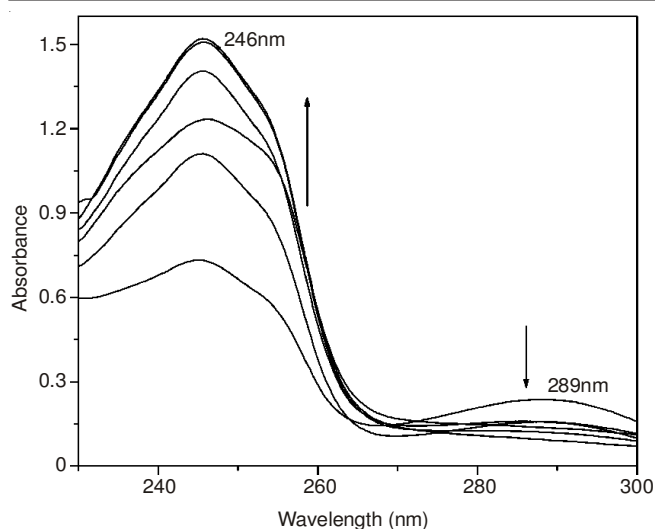
Fig. 1. Increase in the absorption maximum of hydroquinone at 246 nm for oxidation of hydroquinone catalyzed by $Cu_3(BTC)_2$
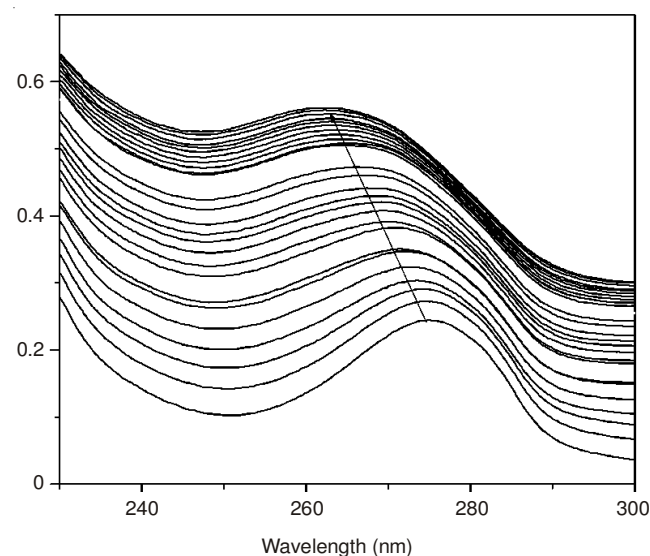

Fig. 2. Violet shift and larger absorbance of the characteristic absorption peak as the reaction time was increased in the oxidation of pyrocatechol catalyzed by $Cu_3(BTC)_2$
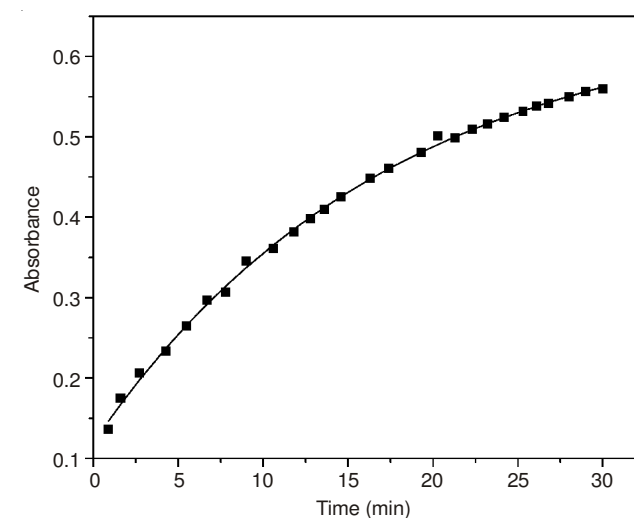

Fig. 3. Plot of A_t *versus* the reaction time t obtained from the experimental data in Fig. 2 (Dots presents the experimental data, and the line shows the fitting results)

Hydroquinone and pyrocatechol catalyzed by $Cu_3(BTC)_2$ using hydrogen peroxide, k_o and k_p are the apparent first-order rate constants for oxidation of hydroquinone and pyrocatechol, respectively. S is selectivity towards *p*-benzoquinone, which can be calculated using k_p/k_o. It can be found that the substrate of $Cu_3(BTC)_2(H_2O)_3$ was 15.43 (T = 35 °C, pH = 7.6 Tris-HCl buffer, [catalyst]/[S] is 0.06, $C_{H_2Q} = 1 \times 10^{-4}$ mol L^{-1}).

Effects of the ratio of the catalyst to H_2Q ([catalyst/substrate]): $Cu_3(BTC)_2$ was selected as a potential candidate in order to investigate the effect of molar ratio [catalyst]/[substrate] on the catalytic selectivity toward hydroquinone. As showing in Table-1, S is increased with the increasing molar ratio of [catalyst]/[substrate]. The oxidation reaction rate of hydroquinone increased dramatically when the molar ratio of $Cu_3(BTC)_2$ to the hydroquinone below 0.12. Further increasing the molar ratio only led to a slight increase in the reaction rate constant, which is due to the effects of catalytic saturation. In the cases of the catalytic oxidation of pyrocatechol on $Cu_3(BTC)_2$, the molar ratio of catalyst to the substrate did not resulted in larger rate constants, the $Cu_3(BTC)_2$ still showed weak catalytic activity to pyrocatechol as the molar ratio is increased. This is ascribed to the steric hindrance and slow movement to the active sites of pyrocatechol. Thus, substrate was increased with the increasing of molar ratio.

TABLE-1 EFFECT OF MOLAR RATIO OF CATALYST/H_2Q ON THE REACTION SELECTIVITY CATALYZED BY $Cu_3(BTC)_2$				
Catalyst	Molar ratio of catalyst/ H_2Q	k_o	k_p	S (k_o/k_p)
$Cu_3(BTC)_2$	0.06	0.599	0.039	15.36
$Cu_3(BTC)_2$	0.12	1.043	0.042	25.03
$Cu_3(BTC)_2$	0.18	1.093	0.032	33.71
[a]T = 35 °C, pH = 7.6, Tris-HCl buffer, $C_{H_2Q} = 1 \times 10^{-4}$ mol L^{-1}.				

Effect of temperature: The oxidation reaction of H_2Q was studied in the *tris*-HCl buffer catalyzed by $Cu_3(BTC)_2$ with molar ratio of 0.06. As shown in Table-2, the rate constant increased remarkably with the increasing reaction temperature in all cases. However, the selectivity hasn't changed but the results are reasonable in theory. With the increasing temperature, it is helpful for the movement of molecular, the rate of adsorption and desorption of the reactants and products must be fast, so the rate of oxidation reaction must be fast. However, the selectivity mainly connected with the active sites. If weight of catalyst is constant, active sites are constant, so the selectivity have no changed seasonally.

TABLE-2 EFFECT OF TEMPERATURE ON THE SELECTIVITY OF CATALYTIC OXIDATION OF H_2Q ON $Cu_3(BTC)_2$				
Catalyst	Temperature (°C)	k_o	k_p	S*(k_o/k_p)
$Cu_3(BTC)_2$	25	0.433	0.028	15.49
$Cu_3(BTC)_2$	30	0.599	0.039	15.36
$Cu_3(BTC)_2$	35	0.893	0.058	15.43
[a][Catalyst]/[S] is 0.06, pH =7.6 Tris-HCl buffer, $C_{H_2Q} = 1 \times 10^{-4}$ mol L^{-1}.				

Conclusion

$Cu_3(BTC)_2$ was very active in selective oxidation of hydroquinone. It has larger selectivity in *Tris*-HCl buffer (pH

= 7.6) at a 0.06 molar ratio of [catalyst]/[S], however, temperature has no influence on the selectivity to hydroquinone.

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