Oxidation of *p*-Cresol to *p*-Hydroxybenzaldehyde with Molecular Oxygen in the Presence of CuMn-Oxide Heterogeneous Catalyst

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Abstract: A high-yield synthesis of *p*-hydroxybenzaldehyde from *p*-cresol and molecular oxygen was achieved over a CuMn-oxide supported carbon catalyst. The reaction parameters such as pressure, stirring speed, reaction temperature, solvent, and the amount of sodium hydroxide in the reaction media were optimized. As a result, a high conversion of *p*-cresol (99%) and a high selectivity to *p*-hydroxybenzaldehyde (96%) were realized at the same time. Catalyst separation and recycling tests clearly showed that the reaction proceeded on the heterogeneous catalyst but not on dissolved species.

Keywords: copper; *p*-cresol; heterogeneous catalysis; *p*-hydroxybenzaldehyde; manganese

Introduction

Hydroxybenzaldehydes are useful raw materials. For example, *p*-hydroxybenzaldehyde is used as an intermediate for making dyes, pharmaceuticals, as well as being a textile auxiliary, and *o*-hydroxybenzaldehyde (salicylaldehyde) is used in perfumery.[1,2] This may be a reason why many papers have dealt with the synthesis of hydroxybenzaldehydes. The formation of *o*- and *p*-hydroxybenzaldehyde using the Reimer–Tiemann reaction from phenol and chloroform was a classical example.[3–5] *p*-Hydroxybenzaldehyde was also produced from phenol and HCN by the Gattermann reaction. Industrially, *p*-hydroxybenzaldehyde was synthesized by side-chain chlorination of *p*-cresol and by subsequent saponification of the resulting dichloromethyl group.[6] The drawbacks of these methods are the employment and the generation of poisonous chemicals.

Direct oxyfunctionalization of cresols at their benzylic positions provides another method for synthesizing hydroxybenzaldehydes.[7–12] Using cobaltous chloride as a homogeneous catalyst, Sharma et al. observed the formation of *p*-hydroxybenzaldehyde from *p*-cresol with 90% conversion and 59% selectivity in methanol as solvent and in the presence of sodium hydroxide.[13] However, its application was restricted due to intricacy in catalyst separation and reuse. Solid heterogeneous catalysts have the advantage of easy recovery and reuse, and are readily amenable to continuous processing.[14–16] Accordingly, zeolite catalysts such as CoAPO-5 and CoAPO-11 were applied to the oxyfunctionalization.[17] Unfortunately, it was found that these CoAPOs were dissolved into the reaction media, and the dissolved species homogeneously catalyzed the reaction.[18,19] Recently, encapsulated cobalt-Schiff base complexes have been employed as a catalyst in the catalytic oxidation of *p*-cresol to *p*-hydroxybenzaldehyde.[20] This study was an interesting attempt to immobilize homogeneous catalysts on solid supports for facilitating catalyst separation, but leaching of the active components was unavoidable in this case.

Cobalt has been known as one of the favorable constituents for a catalyst in selective oxidation of hydrocarbons for a long time.[21,22] In fact, we have reported that cobalt supported on carbon was a highly active and selective catalyst in the catalytic oxidation of *o*-cresol with molecular oxygen to form salicylaldehyde.[23] However, when the cobalt catalyst was adopted in the oxidation of *p*-cresol, the selectivity for *p*-hydroxybenzaldehyde was relatively low. In this report, we present high and selective copper-manganese binary metal oxide catalysts for the oxidation of *p*-cresol by oxygen gas to *p*-hydroxybenzaldehyde (Scheme 1). Except for a few reports,[24,25] copper has never been used in catalytic oxidation of hydrocarbons using molecular oxygen, although copper is found in various metalloproteins, especially in enzymes implicated in the binding of molecular oxygen.[24] Manganese oxide profoundly improved the selectivity for *p*-hydroxybenzaldehyde of copper oxide, as we have reported in preliminary results.[27]

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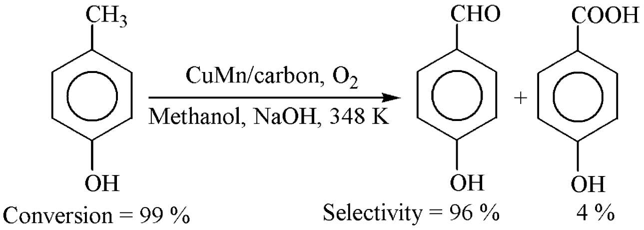
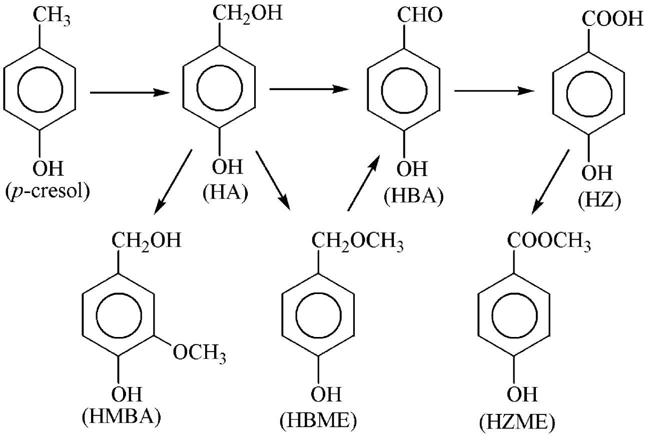


Scheme 1. Catalytic oxidation of *p*-cresol to *p*-hydroxybenzaldehyde.



Scheme 2. The process of catalytic oxidation of *p*-cresol.

Results and Discussion

The catalytic performances of different catalysts in the oxidation of *p*-cresol by molecular oxygen are compared in Table 1. Data were taken at the optimum experimental conditions, which were determined as described in the following sections. Scheme 2 indicates the process of oxidation of *p*-cresol. In addition to the desired product, *p*-hydroxybenzaldehyde (HBA), by-products such as *p*-hydroxybenzoic acid (HZ), *p*-hydroxybenzylmethyl ether (HBME), 4-hydroxy-3-methoxybenzyl alcohol (HMBA) and *p*-hydroxybenzoic acid methyl ester (HZME) were observed. *p*-Hydroxybenzyl alcohol (HA)was not detected.[21] These products can be classified into four groups; one benzyl alcohol-derived compound of *p*-hydroxybenzylmethyl ether, *p*-hydroxybenzaldehyde, two benzoic acid-derived compounds of *p*-hydroxybenzoic acid and *p*-hydroxylbenzoic acid methyl ester, and one ring proton substituted compound of 4-hydroxy-3-methoxybenzyl alcohol.

As seen in Table 1, the reaction did not proceed in the absence of catalyst although autocatalysis by the reactor wall is often recognized in oxidation reactions.[28] In the single component catalysts, Co/carbon exhibited the highest activity, followed by Mn/carbon although similar high selectivities to *p*-hydroxybenzaldehyde were observed on both Co/carbon and Mn/carbon catalysts. Cu/carbon showed to be inferior in both activity and selectivity. However, the addition of manganese into the copper catalyst remarkably improved not only the activity but also the selectivity for *p*-hydroxybenzaldehyde. The CuCo/carbon catalyst, which was reported to be active and selective in the catalytic oxidation of *o*-cresol to salicylaldehyde, was less selective for *p*-hydroxybenzaldehyde production than the CuMn catalyst. The maximal yield of *p*-hydroxybenzaldehyde was observed at Cu/Mn = 4 when the amount of Cu on the active carbon support increased from 1.9 to 7.4 wt % while the amount of Mn remained constant at 1.4 wt %. The best catalyst of the CuMn/carbon series (Cu : Mn = 4 : 1) will be used hereafter for optimization of the experimental conditions.

Table 1. Catalytic oxidation of *p*-cresol by molecular oxygen in the liquid phase.[a]

Catalyst	Molar ratio	Metal wt % in C support	Conversion (mol %)	Product distributions (mol %)		
				HBA[b]	BZ[c]	Others
-[d]	–	–	0	0	0	0
Cu	–	1.3	13	10	15 (3)[e]	75
Mn	–	2.2	19	61	28 (6)	11
Co	–	5.0	38	55	33 (6)	12
CuCo[f]	4:1	10.2	100	52	46 (8)	2
CuMn	5:1	8.7	100	89	10 (1)	1
CuMn	4:1	7.4	99	96	4 (1)	0
CuMn	2:1	4.8	98	95	3 (1)	2
CuMn	1:1	3.5	98	54	24 (5)	22

[a] Reaction conditions: catalyst = 0.6 g, *p*-cresol = 16.0 g, solvent (methanol) = 50 mL, sodium hydroxide = 23.0 g, pressure = 0.3 MPa, temperature = 348 K, time = 3 h, stirring speed = 700 r.p.m.

[b] *p*-Hydroxybenzaldehyde.

[c] *p*-Hydroxybenzoic acid.

[d] No catalyst.

[e] Selectivity for *p*-hydroxybenzoic acid methyl ester in parenthesis.

[f] From Ref.[23]

The amount of the CuMn/carbon catalyst was set to 0.6 g since the catalytic performance such as conversion, product selectivity did not change beyond 0.2 g at the experimental conditions of 16.0 g of *p*-cresol, 50 mL of methanol, 23.0 g of sodium hydroxide, 0.3 MPa oxygen pressure, 348 K temperature, 3 h sampling time, and 700 r.p.m. stirring speed.

Figure 1 shows the time course of catalytic performances in the *p*-cresol oxidation on the CuMn/carbon catalyst at 0.1 MPa, where a portion of the reaction media can be easily withdrawn for the analysis. The yield of *p*-hydroxybenzaldehyde increased with time and reached a plateau at 90% after 13–14 h reaction time. As shown in Table 1, a similar yield of 91% was observed after 3 h reaction time at 0.3 MPa. It is clear from these results that the reaction at 0.3 MPa proceeds more than 3 times faster than that at 0.1 MPa. The higher reaction rate at 0.3 MPa, compared with that at 0.1 MPa, can be easily rationalized from the increase in oxygen solubility, according to Henry's law. An oxygen pressure of 0.3 MPa was used in the following experiments because of experimental limitations of our system.

The catalytic oxidation of *p*-cresol involves three phases: gas, liquid and solid. Then, mass transfer might be the rate-determining step. Figure 2 shows the effect of the stirring speed on the activity and the selectivity. It can be seen that the conversion and the selectivity increased with stirring speed. When the stirring speed reached 700 r.p.m., the 95% yield of *p*-hydroxybenzaldehyde was realized. It is considered that the overall reaction may be affected by gas transferring from bubbles to the liquid phase and by removal of products from the catalyst surface. Moreover, because that the reaction is exothermic, it is rather difficult to control the reaction temperature without stirring. On the other hand, increasing the stirring speed was helpful for quenching developed heat and for improving the selectivity for *p*-hydroxybenzaldehyde. A stirring speed of 700 r.p.m. was used in the following experiments because of experimental limitations of our system.

Figure 3 shows the effect of reaction temperature ranging from 333 K to 353 K on the catalytic performance. As seen, the conversion increased with reaction temperature while the selectivity peaked at 348 K. At a temperature lower than 348 K, the selectivity for the desired product, *p*-hydroxybenzaldehyde, was lowered due to the formation of *p*-hydroxybenzyl methyl ether. On the other hand, at a temperate higher than 348 K, formation of *p*-hydroxybenzoic acid became appreciable. These results may suggest the consecutive oxidation of *p*-cresol *via* *p*-hydroxybenzyl alcohol, *p*-hydroxybenzaldehyde and finally *p*-hydroxybenzoic acid. So the temperature of 348 K has been demonstrated to be satisfactory.

The influence of solvent is summarized in Table 2. No product was observed in water except for tar. When methanol and water were mixed in the volume ratio of 1:1 and employed as solvent, the conversion of *p*-cresol and the selectivity for *p*-hydroxybenzaldehyde increased to 92% and 61%, respectively. Methanol among the four solvents tested was the best solvent in the catalytic oxidation of *p*-cresol. One of the reasons for the high yields of *p*-hydroxybenzaldehyde in methanol and ethanol should come from the higher solubility of oxygen in methanol and ethanol than that in water; oxygen solubilities at 1 atmosphere in 1 mL solvent at 293 K are 0.031, 0.220 and 0.256 mL for water, ethanol and methanol, respectively.[29] In the course of mass transfer, methanol is helpful for *p*-cresol to approach the catalyst surface and for *p*-hydroxybenzaldehyde to diffuse into

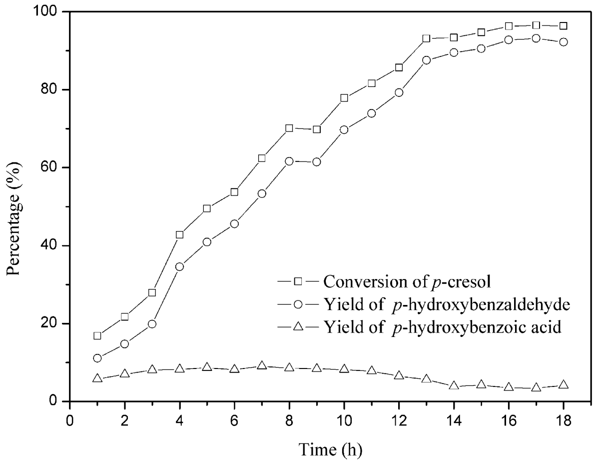


Figure 1. Time course of the reaction at 0.1 MPa. Reaction conditions: catalyst (CuMn/carbon, Cu:Mn = 4:1) = 0.6 g, *p*-cresol = 16.0 g, solvent (methanol) = 50 mL, sodium hydroxide = 23.0 g, temperature = 348 K, stirring speed = 700 r.p.m.

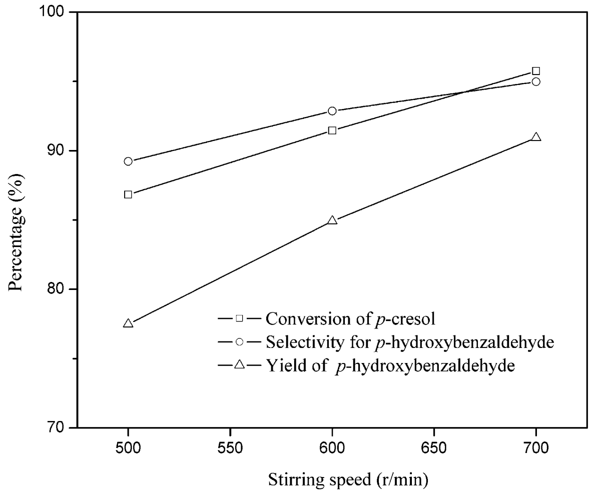


Figure 2. Effect of stirring speed on the catalytic activity Reaction conditions: catalyst (CuMn/carbon, Cu:Mn = 4:1) = 0.6 g, *p*-cresol = 16.0 g, solvent (methanol) = 50 mL, sodium hydroxide = 23.0 g, pressure = 0.3 MPa, temperature = 348 K, time = 3 h.

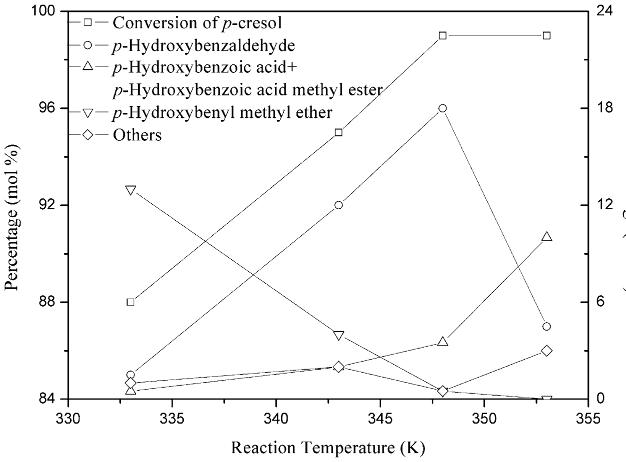


Figure 3. Influence of reaction temperature on catalytic performance. Reaction conditions: catalyst (CuMn/carbon, Cu:Mn = 4:1) = 0.6 g, *p*-cresol = 16.0 g, solvent (methanol) = 50 mL, sodium hydroxide = 23.0 g, pressure = 0.3 MPa, time = 3 h, stirring speed = 700 r.p.m.

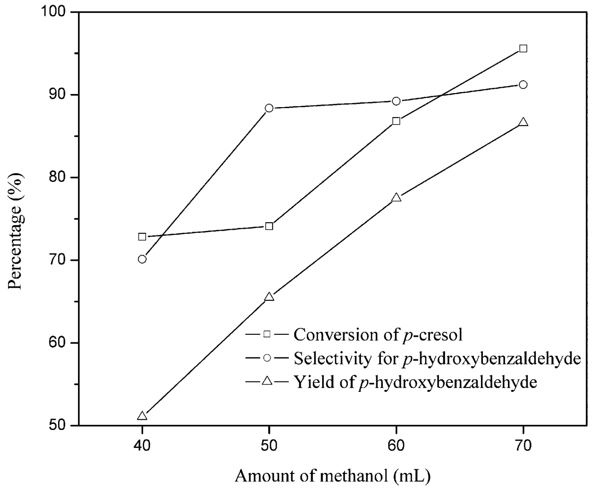


Figure 4. Influence of the amount of solvent. Reaction conditions: catalyst (CuMn/carbon, Cu:Mn = 4:1) = 0.6 g, *p*-cresol = 16.0 g, sodium hydroxide = 23.0 g, pressure = 0.3 MPa, temperature = 348 K, time = 3 h, stirring speed = 700 r.p.m.

the solvent. Otherwise water, as one of the oxidation products, offers resistance to the forward reaction kinetically.[30,31]

The influence of the amount of methanol was investigated to minimize solvent use. The results are depicted in Figure 4. The yield of *p*-hydroxybenzaldehyde increased to 87% from 51% while the methanol amount varied from 40 to 70 mL. More methanol could help to achieve better temperature control and is beneficial for product diffusion. Another reason for the higher yield at higher solvent volume may be the increase of the oxygen supply due to the use of a larger amount of solvent and lower NaOH concentration at the higher amount of methanol. Both are beneficial for increasing the amount of oxygen in solution.

It has been reported in the literature[32,33] that sodium hydroxide was essential for oxidation at the benzylic position of phenols. The desired product *p*-hydroxybenzaldehyde was not observed in an experiment without sodium hydroxide. Figure 5 shows the effect of the molar ratio of NaOH to *p*-cresol on the conversion and the selectivity for *p*-hydroxybenzaldehyde. A maximum selectivity for *p*-hydroxybenzaldehyde was obtained at the molar ratio 4:1 while *p*-cresol conversion was more than 95% at molar ratios higher than 2. With further increases of the NaOH to *p*-cresol ratio, the selectivity declined sharply.

After 9 h of reaction at 348 K and 0.1 MPa, the CuMn catalyst was separated on a Büchner funnel at 348 K and the reaction was continued using the filtrate under the same conditions, in a similar manner as in the litera-

Table 2. Influence of solvent in the oxidation of *p*-cresol.[a]

Solvent	Conversion (mol %)	Yield of HBA[b] (mol %)
H_2O	17	0
$CH_3OH + H_2O$ (1:1)[c]	92	61
CH_3CH_2OH	95	71
CH_3OH	98	96

[a] Reaction conditions: catalyst (CuMn/carbon, Cu: Mn = 4:1) = 0.6 g, *p*-cresol = 16.0 g, solvent = 50 mL, sodium hydroxide = 23.0 g, pressure = 0.3 MPa, temperature = 348 K, time = 3 h, stirring speed = 700 r.p.m.

[b] *p*-Hydroxybenzaldehyde.

[c] Volume ratio.

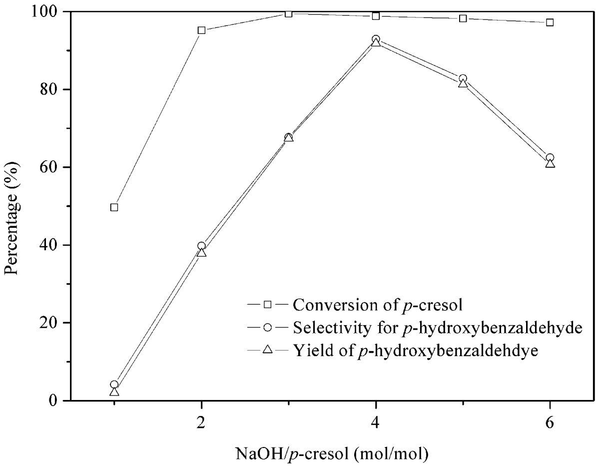


Figure 5. Influence of the molar ratio of NaOH to *p*-cresol. Reaction conditions: catalyst (CuMn/carbon, Cu:Mn = 4:1) = 0.6 g, *p*-cresol = 16.0 g, solvent (methanol) = 50 mL, pressure = 0.3 MPa, temperature = 348 K, time = 3 h, stirring speed = 700 r.p.m.

ture.[34] This experiment was conducted to determine whether the reaction was promoted by the heterogeneous catalyst or by a homogeneous catalyst of dissolved species. In Figure 6, the conversion was plotted against time-on-stream for the results before catalyst separation and after catalyst separation, together with 18 h continuous experiment with catalyst as a reference experiment. The figure clearly shows that no reaction was observed from the filtrate and so the reaction proceeds under heterogeneous catalysis. Furthermore, the re-usability of catalyst was tested. In this experiment, the oxidation reaction was conducted at 348 K and 0.3 MPa in an autoclave for 3 h and the catalyst was separated. The separated catalyst was washed with deionized water to neutrality and dried at 393 K for 3 hours. This catalyst was applied for a 2nd experiment by adding fresh *p*-cresol. Similarly a 3rd experiment was conducted. Results were conversion = 100%, selectivity for *p*-hydroxybenzaldehyde = 93% for the 2nd experiment and conversion = 100%, selectivity for *p*-hydroxybenzaldehyde = 88% for the 3rd experiment, showing a minor drop in selectivity. When the catalysts were regenerated under the same conditions as washing by methanol and calcination at 673 K, the catalytic activity was completely recovered to conversion = 98% and selectivity = 94%, indicating that there is a small amount of substances strongly adsorbed on the catalyst surface.

Conclusion

The results can be summarized as follows.

1. Copper-manganese bimetallic oxide-supported on active carbon was found to be effective in the catalytic oxidation of *p*-cresol to *p*-hydroxybenzaldehyde. After optimization of the reaction conditions, 99% conversion of *p*-cresol and 96% selectivity for *p*-hydroxybenzaldehyde were achieved at 0.3 MPa oxygen pressure, 348 K temperature, NaOH/*p*-cresol mole ratio of 4, Cu/Mn mole ratio of 4 and in methanol as a solvent.
2. The activity obeys almost first-order kinetics with respect to oxygen concentration. We found a big difference in catalytic activity between water and methanol. This result was also rationalized from the solubility of oxygen in these solvents.
3. A large amount of alkali, NaOH, is needed for the reaction to be highly active and selective.
4. The catalyst was re-usable after washing and drying. The catalyst can be separated from the reaction mixture by simple filtration. Furthermore, the filtrate after removing the catalyst did not show any appreciable reaction, indicating that the reaction was catalyzed on the heterogeneous solid catalyst.

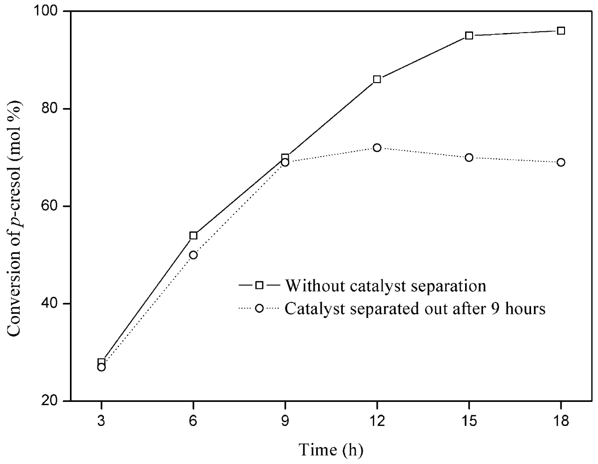


Figure 6. Influence of catalyst separation. Reaction conditions: catalyst (CuMn/carbon, Cu:Mn = 4:1) = 0.6 g, *p*-cresol = 16.0 g, solvent (methanol) = 50 mL, sodium hydroxide = 23.0 g, pressure = 0.1 MPa, temperature = 348 K, stirring speed = 700 r.p.m.

Experimental Section

Reagents

All chemicals were of analytical grade and were purchased from commercial sources. Oxygen supplied in a high-pressure cylinder was used without further treatment.

Preparation of Catalysts

Catalysts were prepared using a commercial activated carbon (60–80 mesh, sorption capacity 1.4 mL g^{-1}, specific surface area 1100 m^2 g^{-1}) as support. The support was impregnated with an aqueous solution of copper and/or manganese nitrates according to the ratio and metal weight of the catalysts, using the incipient wetness method. After impregnation, the samples were first dried at 393 K and then calcined at 673 K in a vacuum quartz tube to afford the oxides. The ratio and metal weight of the catalysts are listed in Table 1.

Catalytic Oxidation of *p*-Cresol

The oxidation reactions were carried out in a stirred autoclave (Parr Instrument, 600 mL, Series 4560, USA) equipped with a motor drive magnetically coupled to an internal turbine-type impeller, a speedometer, a thermocouple, a pressure gauge and a water-cooling coil. In a typical reaction, *p*-cresol (16.0 g, 0.15 mol), sodium hydroxide (23.0 g, 0.58 mol), methanol (50 mL) and catalyst (0.6 g) were placed in the reactor and were mixed with the impeller. The reactor was heated up to a set temperature by an electric furnace. After the desired temperature was reached, oxygen was charged to the reactor through a dip tube. The pressure was kept constant by supplying oxygen gas during the reaction. The reaction was terminated when the required time had elapsed.

Products Analysis

About 0.5 mL of sample withdrawn from the reaction mixture was acidified by hydrochloric acid (1:1, volume ratio) to pH = 2 ~ 3 and diluted with methanol. The diluted sample was analyzed on an HPLC (Shimadzu, Model LC-9A, Chrompak C18 15 cm column, UV 254 nm). Authentic standard samples were used for identification of the products. The *p*-cresol conversion and product distributions were evaluated from relative sensitivity factors from calibration curves of all reaction products, employing phenol as internal standard. GC-MS was used to detect by-products. The definition of conversion and selectivity are as follows: conversion = amount of reactant consumed divided by the amount of reactant charged; selectivity = the amount of a particular product formed divided by the total amount of reactant consumed. It should be noted that the sample should be analyzed immediately after acidification to avoid autoxidation.

Separation of *p*-Hydroxybenzaldehyde

The reaction mixture was filtered or centrifuged to remove catalyst, and then distilled under reduced pressure to remove solvent. The residue was acidified by hydrochloric acid (1:1, volume ratio) to pH = 2 ~ 3. The solution was chilled to a temperature of 273 – 278 K and maintained at the temperature for 10 h or longer. During this cooling procedure, the desired product *p*-hydroxybenzaldehyde crystallized. The crystals were filtered off and washed with chilled water to remove encapsulated *p*-cresol and by-products. The purity was more than 99% from HPLC analysis. The yield was 92%.

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