

## Copper and manganese: two concordant partners in the catalytic oxidation of *p*-cresol to *p*-hydroxybenzaldehyde

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Copper and manganese were found to be two concordant partners in the synthesis of *p*-hydroxybenzaldehyde from *p*-cresol; under mild conditions, this research realised 95.6% selectivity for *p*-hydroxybenzaldehyde at 98.5% conversion of *p*-cresol.

Catalytic functionalization of the relatively inert hydrocarbon C–H bond under mild conditions is one of the most desirable reactions and remains a challenge for chemists.<sup>1</sup> Employing *p*-cresol as feedstock, researchers have developed several methods to obtain *p*-hydroxybenzaldehyde. Besides the chlorination route, homogeneous<sup>2</sup> and heterogeneous<sup>3</sup> catalysts are extensively used, among which cobalt is most favoured. We also found that cobalt is an excellent catalyst for C–H bond activation in the oxidation of *o*-cresol to salicylaldehyde.<sup>4</sup> However, when the catalyst (copper and cobalt impregnated on activated carbon) was used in the oxidation of *p*-cresol, the selectivity for *p*-hydroxybenzaldehyde was relatively low. Generally cobalt oxides possess an extremely high oxidative reactivity and manganese dioxide has a lower, although still rather high, activation ability.<sup>5</sup> Considering the difference in the two substrates, we chose manganese instead of cobalt in the catalyst preparation to improve the selectivity for *p*-hydroxybenzaldehyde in the oxidation of *p*-cresol. The results are quite impressive.

To the best of our knowledge, there are no reports on the heterogeneously catalysed oxidation of *p*-cresol to *p*-hydroxybenzaldehyde over copper and manganese bimetallic oxide catalysts. Compared to organometallic catalysts<sup>2b</sup> and zeolites,<sup>2c,3c</sup> the CuMn/C catalyst is less demanding, economical in preparation, and suitable for large-scale production. The catalyst was prepared using a commercial activated carbon (specific surface area 1100 m<sup>2</sup> g<sup>-1</sup>) as support. The support was impregnated with an aqueous solution of copper and/or manganese nitrates 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.

The catalytic oxidation reactions were carried out in a 600 mL capacity stirred autoclave (Parr Instruments, USA) under an oxygen pressure of 0.3 MPa with analysis by liquid chromatography (HPLC, Shimadzu liquid chromatograph, Model LC-9A, equipped with a Chrompak C18 15 cm column, UV 254 nm). Authenticated standard samples were used to determine the identity of the products and for calibration. The total conversion<sup>†</sup> and product distribution were evaluated with calibration curves.

The performance of different catalysts for *p*-cresol oxidation was studied under the same reaction conditions (Table 1). A blank run without catalyst gave no products. Single component catalysts exhibit lower activity and selectivity than bimetallic catalysts; addition of cobalt increases the selectivity for acid whilst introduction of manganese can remarkably improve the selectivity for *p*-hydroxybenzaldehyde. Changing the weight content of manganese in the CuMn/C catalysts has little effect on the conversion of *p*-cresol. Variations in performance are partly due to the difference in the activation energies of

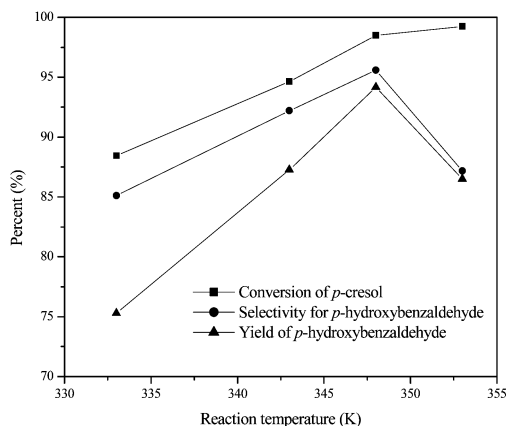
Table 1 Catalytic oxidation of *p*-cresol<sup>a</sup>

Catalysts	Molar ratio	Metal weight (wt%)	Con-version (mol%)	Product distribution (mol%)		
				PHB <sup>b</sup>	PHBA <sup>c</sup>	Others
— <sup>d</sup>	—	—	0	0	0	0
Cu/C	—	1.3	12.8	9.5	11.8	78.7
Mn/C	—	2.2	18.7	61.2	21.9	16.9
Co/C	—	5.0	37.9	54.8	27.2	18.0
CuCo/C <sup>e</sup>	4:1	10.2	99.5	52.3	38.4	9.3
CuMn/C	5:1	8.7	99.9	88.7	8.6	2.7
CuMn/C	4:1	7.4	98.5	95.6	2.6	1.8
CuMn/C	2:1	4.8	97.7	94.9	1.8	3.3
CuMn/C	1:1	3.5	98.0	54.4	19.2	26.4

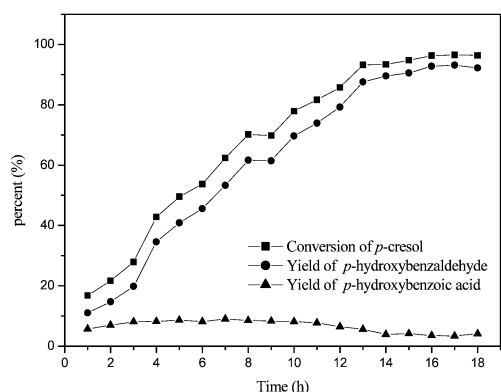
<sup>a</sup> Reaction conditions: catalyst = 0.6 g, *p*-cresol = 16.0 g, solvent (methanol) = 50 mL, sodium hydroxide = 23.0 g, pressure = 0.3 MPa, time = 3 h, temperature = 348 K. <sup>b</sup> *p*-Hydroxybenzaldehyde. <sup>c</sup> *p*-Hydroxybenzoic acid. <sup>d</sup> No catalyst. <sup>e</sup> Ref. 4.

exchange in molecular oxygen. Low activation energies result in a high oxygen supply ability. The literature data<sup>5b</sup> on oxygen isotopic exchange give the sequence of oxygen supply ability as: Co<sub>3</sub>O<sub>4</sub> > MnO<sub>2</sub> > CuO. The oxidation reaction requires a reasonable activation match of the C–H and oxygen bond *via* interaction with the catalyst active site. The electrophilic oxygen (O<sup>-</sup>, O<sub>2</sub><sup>-</sup>) tends to accumulate on the surface of the cobalt catalyst, which enhances the probability of electrophilic attack on the C=O bond of *p*-hydroxybenzaldehyde. Manganese acting as an assistant to copper improves the oxygen exchange between bulk phase and the catalyst surface by accelerating the valence transformation of copper. The concentration of electrophilic oxygen is kept at a relatively low level thus avoiding oxidation of *p*-hydroxybenzaldehyde. Activation of the C–H bond happens on active sites by virtue of hydrogen abstraction from the methyl group of *p*-cresol. If one C–O bond is formed, the product is alcohol, and if one C–H bond in the adsorbed benzyl species is activated and dissociates, another C–O bond will be formed and aldehyde is produced. During the oxidation of *p*-cresol, copper and manganese work together well as two concordant partners to realise the reasonable match of C–H and oxygen bond activation.

The influence of reaction temperature on the conversion of *p*-cresol was investigated from 333 to 353 K (Fig. 1). It can be seen that the yield of *p*-hydroxybenzaldehyde peaks at 348 K. A further increase in reaction temperature aggravates the oxidation of *p*-hydroxybenzaldehyde to *p*-hydroxybenzoic acid. The change of *p*-cresol, *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid with time was investigated (Fig. 2). It indicates that the conversion of *p*-cresol and the yield of *p*-hydroxybenzaldehyde improve rapidly up to 14 hours. The conversion of *p*-hydroxybenzaldehyde to *p*-hydroxybenzoic acid is inhibited by the catalyst. A slight decrease in the yield of acid occurs after a 9 h run due to the reaction of acid with methanol to form methyl-*p*-hydroxybenzoate which was detected by GC-MS analysis. Sodium hydroxide is essential for the reaction for two reasons: firstly, it reacts with the hydroxyl of *p*-cresol and prevents oxidation on the benzene ring; secondly, it is generally



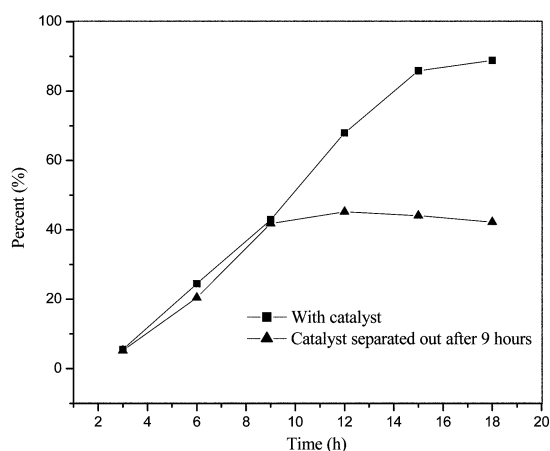
**Fig. 1** Influence of the reaction temperature on catalytic performance. Reaction conditions: catalyst (CuMn/C, Cu:Mn = 4:1) = 0.6 g, *p*-cresol = 16.0 g, solvent (methanol) = 50 mL, sodium hydroxide = 23.0 g, pressure = 0.3 MPa, time = 3 h.



**Fig. 2** Influence of the reaction time on catalytic performance. Reaction conditions: catalyst (CuMn/C, 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.

believed that acid media lead to hypo oxidation and base media are beneficial for selective oxidation.

Catalyst separation tests were carried out by the previously published method<sup>6</sup> and the results are shown in Fig. 3. ‡ It can be seen that the reaction is almost completely suspended after catalyst separation. Fine catalyst powder penetrating through the filter paper may cause the slight yield increase of *p*-hydroxybenzaldehyde. The catalyst was also recycled to check the stability (first run, conversion = 100%, selectivity for *p*-hydroxybenzaldehyde = 92.7%; second run, conversion = 100%, selectivity for *p*-hydroxybenzaldehyde = 88.2%). The catalyst was washed with deionized water to neutral pH and then dried at 393 K for 3 hours before the second run. When the catalysts were washed with methanol and calcined at 673 K, the recycled catalyst performed as well as the fresh catalyst. No more runs were carried out because of the decrease in catalyst recovered each time. The activated carbon is fragile under solution reaction conditions with high-speed stirring. Future studies will concentrate on improving catalyst mechanical



**Fig. 3** Influence of catalyst separation on the yield of *p*-hydroxybenzaldehyde. Reaction conditions: catalyst (CuMn/C, 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.

strength by changing preparation methods toward large-scale applications.

In summary, copper and manganese were found to be two concordant partners in the catalytic oxidation of *p*-cresol to *p*-hydroxybenzaldehyde. Under mild conditions, this research realised 95.6% selectivity for *p*-hydroxybenzaldehyde at 98.5% conversion of *p*-cresol.

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## Notes and references

† The definition of conversion and selectivity are as follows: conversion = moles of *p*-cresol consumed/moles of *p*-cresol used  $\times$  100%; selectivity = moles of product/moles of *p*-cresol consumed  $\times$  100%.

‡ The procedure for the catalyst separation test was as follows: the reaction was carried out at 348 K (0.1 MPa pressure) and, after 9 h, immediately transferred from a flask to a Buchner funnel (also at 348 K). The reaction was then continued using the filtered reaction mixture under the same conditions as pre-separation.

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