

# Hydroxylation of phenol catalyzed by copper Keggin-type heteropoly compounds with hydrogen peroxide

Hanpeng Zhang, Xiaoming Zhang, Yong Ding, Liang Yan, Tong Ren and Jishuan Suo\*

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, The Chinese Academy of Sciences, Lanzhou 730000, China.

E-mail: jssuo@ns.lzb.ac.cn; Fax: +86 931 827 7787; Tel: +86 931 827 5727

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**A novel catalytic process for the oxidation of phenol to dihydroxybenzene with hydrogen peroxide was developed in which copper-12-silicotungstic acid was used as catalyst in aqueous solution. The maximal conversion of phenol is ca. 39%, which is much higher than the results in acetonitrile reported previously.**

Hydrogen peroxide as an oxidant for the hydroxylation of phenol is currently the most interesting way for producing dihydroxybenzene,<sup>1–5</sup> the reason being its ready availability, low cost and the environmentally friendly by-products produced (water and molecular oxygen). Silica–alumina<sup>6–9</sup> and titanium-containing molecular sieves have been widely studied and used as catalysts for the hydroxylation of phenol, however, their somewhat complicated synthetic conditions and high cost limit their uses.<sup>2,4–6</sup> Heteropoly compounds are effective catalysts for various oxidation reactions, because their redox and acidic properties can be controlled at the atomic/molecular levels by changing the constituent elements.<sup>10–13</sup> Keggin-type heteropoly acids have been investigated extensively for their easy synthesis, thermal stability and low cost.<sup>14</sup> Recently, Keggin-type  $Q_3PMo_mW_{12-m}O_{40}$  or  $Q_{3+x}PM_{12-x}V_xO_{40}$  ( $x = 0–3$ ,  $m = 0–6$ ,  $M = Mo, W$ ) and Dawson-type heteropoly acids have been used as catalysts for the hydroxylation of phenol with hydrogen peroxide as oxidant;<sup>3,15</sup> the reactions were carried out in acetonitrile and the conversion of phenol was only 10–15%. Transition metal salts or oxides also can catalyze the oxidation of phenol to dihydroxybenzene but the results were not satisfactory.<sup>16–18</sup> Thus, the development of more feasible and environmentally friendly processes for the hydroxylation of phenol is desirable. In this study, a novel catalytic system has been developed by combining a Cu(II) salt and 12-silicotungstic acid ( $H_4SiW_{12}O_{40}$ , denoted as  $SiW_{12}$ ); it

was found that this catalytic system exhibits good activity for the hydroxylation of phenol to catechol with hydrogen peroxide in aqueous solution.

At first,  $CuCl_2$  was used as the copper source, and it was combined with different kinds of heteropoly acids having a Keggin-type structure such as  $SiW_{12}$ ,  $H_4SiMo_{12}O_{40}(SiMo_{12})$ ,  $H_3PW_{12}O_{40}(PW_{12})$  and  $H_3PMo_{12}O_{40}(PMo_{12})$  to prepare the catalytic system. The catalytic results are listed in Table 1. When pure  $SiW_{12}$  was used as the catalyst, the conversion of phenol was only 8.51% and the main product was benzoquinone. Although the conversion reached 24.63% when  $CuCl_2$  was used as the catalyst (thus, the reaction changes to a Fenton reaction catalyzed by Cu),<sup>9,19</sup> nearly equal amounts of hydroquinone and catechol were obtained, which will cause difficulty in the separation of the products. When  $CuCl_2$  was combined with  $SiW_{12}$  to form a new catalytic system, the catalytic performance improved greatly with respect to that of the separate components (38.67% conversion of phenol with a selectivity of 62.66% to catechol). The catalytic action of transition metals combined with heteropoly acids has been observed before: aqueous acidic solution of heteropoly acids associated with Pd(II) or Rh(III) salts can catalyze the oxidation of unsaturated substrates to ketones.<sup>20,21</sup> Although  $SiMo_{12}$ ,  $PW_{12}$  and  $PMo_{12}$  have the same Keggin structure as  $SiW_{12}$ , their catalytic activities when they were combined with  $CuCl_2$  in the same manner were very low. The activity of  $SiW_{11}Cu$  was also very low. The acidity order of these heteropoly compounds is  $PW_{12} > SiW_{12} > PMo_{12} > SiMo_{12} > SiW_{11}Cu$ ; this suggests that the catalytic performance is closely related to the co-existence of Cu(II), Si, and W in the appropriate acidity range. Although the mono-copper-substituted silicotungstic acid's ( $SiW_{11}Cu$ ) selectivity to catechol was over 70%, the conversion of phenol was lower than that of  $CuCl_2 + SiW_{12}$  (16.28% *vs.*

**Table 1** Catalytic activity of the different catalysts studied

Catalyst	Phenol conv. (%)	Selectivity of isomers <sup>a</sup> (%)			H <sub>2</sub> O <sub>2</sub>	
		HQ	CAT	BQ	Conv. (%)	Select. (%)
$SiW_{12}$	8.51	23.02	30.54	46.46	20.51	23.19
$CuCl_2$	24.63	43.84	45.14	10.45	41.83	24.69
$CuCl_2 + SiW_{12}^b$	38.67	17.83	62.66	16.08	50.43	32.96
$CuCl_2 + SiMo_{12}^b$	3.00	13.74	31.70	54.48	89.36	1.98
$CuCl_2 + PW_{12}^b$	0.54	54.26	—	45.78	90.96	0.33
$CuCl_2 + PMo_{12}^b$	0.26	54.23	—	45.78	17.58	0.855
$SiW_{11}Cu$	16.28	13.93	72.14	13.93	48.57	14.57
$Cu_2SiW_{12}O_{40}$	1.13	19.71	56.89	23.39	74.29	0.72

<sup>a</sup> HQ = hydroquinone, CAT = catechol, BQ = benzoquinone. <sup>b</sup> Cu content: 2%.

**Table 2** Influence of the copper source in the Cu(II) + SiW<sub>12</sub> catalytic systems (1% Cu)

Copper source	Phenol conv. (%)	Selectivity of isomers <sup>a</sup> (%)		
		HQ	CAT	BQ
Cu(NO <sub>3</sub> ) <sub>2</sub>	27.32	16.58	67.35	12.17
CuCl <sub>2</sub>	26.00	14.40	66.79	14.24
Cu(CH <sub>3</sub> COO) <sub>2</sub>	25.68	19.65	66.92	9.98
CuSO <sub>4</sub>	23.55	20.19	66.49	10.30
CuCl	14.42	16.58	67.35	12.17

<sup>a</sup> HQ = hydroquinone, CAT = catechol, BQ = benzoquinone.

38.67%), indicating that the incorporation of Cu into the framework of SiW<sub>12</sub> does not enhance its catalytic performance.

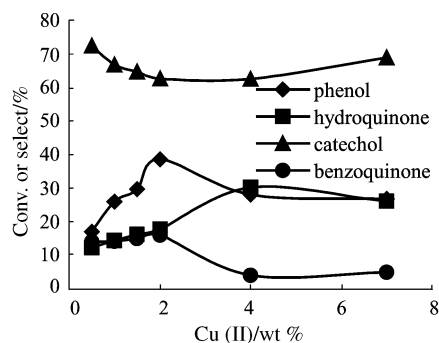
The conversion of H<sub>2</sub>O<sub>2</sub> as well as the selectivity to the products (HQ + CAT + BQ) are also listed in Table 1. For those catalysts with low activities (such as CuCl<sub>2</sub> + PW<sub>12</sub>), although the conversion of H<sub>2</sub>O<sub>2</sub> is very high (90.96%), the selectivity to the products is very low (0.33%). Furthermore, it was observed that the H<sub>2</sub>O<sub>2</sub> began to decompose rapidly as soon as it was added into the reaction mixture at a given temperature. This suggests that the low activities of these catalysts is mainly due to the quickly decomposition of H<sub>2</sub>O<sub>2</sub>. In contrast, the decomposition of H<sub>2</sub>O<sub>2</sub> was slow for those catalysts with high phenol conversion (such as CuCl<sub>2</sub> + SiW<sub>12</sub>), and the efficiency of H<sub>2</sub>O<sub>2</sub> was relatively higher.

Different kinds of copper salts were used as the copper precursor in the Cu(II) + SiW<sub>12</sub> system; a comparison of the catalytic results is shown in Table 2. The highest conversion was obtained when copper nitrate was used, but the influence of the anions in the copper salts on the activities is not notable. Compared to Cu<sup>+</sup>, Cu<sup>2+</sup> leads to a higher conversion of phenol, while the selectivity to catechol is over 65% with either cation.

Fig. 1 shows the influence of the copper content in the catalytic system on the activity and selectivity of phenol oxidation. The conversion of phenol achieved its maximum value (ca. 39%) when the amount of copper was ca. 2%. The selectivity to hydroquinone exhibited a similar trend with copper content, but the best result was obtained at a level of 4%. The influence of copper content on the selectivity to catechol was not notable. The amount of benzoquinone decreased upon increasing the copper content, indicating that high copper levels can inhibit the further oxidation of hydroquinone.

The activity of the catalytic system Cu(II) + SiW<sub>12</sub> was tested in different solvents. It was found that water was the best solvent, the activities in acetonitrile, acetic acid, and other solvents being much lower.

In conclusion, the combination of Cu(II) with SiW<sub>12</sub> can offer a good catalytic system for the hydroxylation of phenol

**Fig. 1** The influence of the copper content in the catalytic system CuCl<sub>2</sub> + SiW<sub>12</sub>.

with hydrogen peroxide in aqueous solution. It provides an alternative and environmentally benign process for the oxidation of phenol to dihydroxybenzene. A systematic study, including the detailed reaction mechanism, is still in progress.

## Experimental

The heteropoly acids were prepared by standard methods<sup>22,23</sup> and the catalyst was prepared as follows. SiW<sub>12</sub> was dissolved in water, controlled amounts of the Cu(II) salt was added and the mixture was stirred at room temperature for 4 h, then dried at 120 °C. The sample so-obtained is designated as Cu + SiW<sub>12</sub>-H<sub>8</sub>SiW<sub>11</sub>CuO<sub>40</sub>(SiW<sub>11</sub>Cu) was synthesized by a slight modification of the method reported in ref. 24. Cu<sub>2</sub>SiW<sub>12</sub>O<sub>40</sub> was prepared by the reaction of H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> and CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>·xH<sub>2</sub>O in the stoichiometric ratio. The formation of the Keggin structure and the compositions were confirmed by IR (Nicolet 10 DX-FTIR spectrometer, 0.5 mm KBr pellets containing 2.5 mass% sample), XRD [D/Max 2400 Rigaku diffractometer, Cu-K $\alpha$  radiation,  $\lambda$  = 0.1542 nm, scan speed 2° (2 $\theta$ ) min<sup>-1</sup>], <sup>31</sup>P NMR (Varian Unity-400 NMR spectrometer, D<sub>2</sub>O as the solvent, 85% H<sub>3</sub>PO<sub>4</sub> as the reference standard), and elemental analysis (ARL 3520 ICP atomic emission spectrometer).

The catalytic reaction was performed in a 100 ml flask equipped with condenser, magnetic stirrer, and oxygen collector. In a typical reaction, 2.0 g phenol was dissolved in 12 ml water, and 0.2 g catalyst was added. The mixture was heated to 70 °C under stirring, then 4.5 ml H<sub>2</sub>O<sub>2</sub> (30%) was added dropwise to start the reaction. After 4.5 h, the reaction was stopped, the product was homogenized in acetone and analyzed with a 7890II gas chromatograph (Shanghai, China), using cyclohexanone as the internal standard.

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