

# Catalytic activity of $K_{0.5}(NH_4)_{5.5}[MnMo_9O_{32}] \cdot 6H_2O$ in phenol hydroxylation with hydrogen peroxide

Shen Lin\*, Ying Zhen, Shi-Ming Wang, Yu-Mei Dai

*Department of Chemistry, Fujian Normal University, Fuzhou 350007, Fujian, People's Republic of China*

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## Abstract

Catalytic properties of the title heteropoly compound,  $K_{0.5}(NH_4)_{5.5}[MnMo_9O_{32}] \cdot 6H_2O$ , were studied in homogeneous phenol hydroxylation with 30% hydrogen peroxide as oxidant. The effects of the amount of the title compound and  $V_2O_5$ , temperature, time, solvent and phenol/ $H_2O_2$  molar ratio on catalytic activity were investigated. The experimental results indicated that the title heteropoly complex in the presence of  $V_2O_5$  was an effective catalyst for the phenol hydroxylation with hydrogen peroxide. Under optimum conditions, the conversion of phenol was 45.04%; the yield and the selectivity of hydroquinone were 38.64% and 85.79%, respectively. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Phenol hydroxylation; Diphenol; Manganese(IV) complex; Hydrogen peroxide; Homogeneous catalysis

## 1. Introduction

Diphenols (DBH), i.e., catechol (CAT) and hydroquinone (HQ), are important chemical materials in industrial chemistry. DBH from phenol hydroxylation with  $H_2O_2$  as the oxidant has become one of the promising approaches in the 21st century because it demands for the simple techniques and produces little environmental pollution. The catalysts reported to be used in phenol hydroxylation to date are (1) molecular sieves [1–8], (2) heteropoly compounds of the

Dawson structural type: molybdovanadophosphate and tungstovanadophosphate [9,10], (3) copper–aluminum hydrotalcite-like compounds [11] and (4) metal complexes [12–14] etc. The catalysts mentioned above have some catalytic activity for phenol hydroxylation, but the reaction lacks industrial value because of their relatively low yield. Therefore, catalysts with high activity and high selectivity have become an important target in this field. In our study,  $K_{0.5}(NH_4)_{5.5}[Mn(IV)Mo_9O_{32}] \cdot 6H_2O$  (hereafter denoted Mn(IV)Mo) in the presence of  $V_2O_5$  was selected as a catalyst to catalyze phenol hydroxylation. With methanol as solvent, pH = 6.0, phenol/ $H_2O_2$  (molar ratio) = 1:1,  $T = 343$  K and time = 5 h, the conversion of phenol is 45.04% and the yield of HQ is

\* Corresponding author.

E-mail address: shenlin@fjtu.edu.cn (S. Lin).

38.64% ,which exceed that of the reported cases now available.

## 2. Experimental

### 2.1. Preparation of Mn(IV)Mo complex

KMnO<sub>4</sub> (2.5 mmol) and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> · 4H<sub>2</sub>O (3.2 mmol) were dissolved in water separately, and then the two solutions were mixed. pH value was adjusted to 4.0 by 2 mol/l HNO<sub>3</sub> or by saturated NH<sub>4</sub>OAc solution. The mixture was kept in a constant temperature bath at 328 K for 4 h, and was then filtrated. The filtrate was held at room temperature for a few hours to give red crystals.

Determination of the crystal structure of the title complex was performed by an Enraf-Nonius CAD4 diffractometer. ESR spectra were recorded on a Bruken-ER-420 spectrometer. IR spectrum was measured on a Perkin-Elmer 983G spectrometer. DTA-TG analysis was made on a DT-40 thermal system.

### 2.2. Examination of catalytic activity for phenol hydroxylation

Hydroxylation was carried out in a round-bottomed flask equipped with a stirrer, a reflux condenser and a thermostat. Phenol, solvent and catalyst were added successively into the reactor. The H<sub>2</sub>O<sub>2</sub> was added at the set temperature. The volume of O<sub>2</sub> was recorded by gas burette. Product analysis was performed by Shimadzu LC-6A liquid chromatograph, with a column of C<sub>8</sub> at room temperature, 150 kg/cm<sup>2</sup> pressure of the column, methanol and water (7:3) as flow phase, UV-Vis detector. The internal standard method was used, with cyclohexanone as the internal standard substance. At the conditions mentioned above, only HQ, CAT and BQ can be defined qualitatively and quantitatively. The calculation of the phenol conversion and the product yield was based on the amount of phenol added.

## 3. Results and discussion

### 3.1. Characterization of the Mn(IV)Mo complex

The results of the elemental analysis are as follows: Anal. Calc. For H<sub>34</sub>K<sub>0.5</sub>MnMo<sub>9</sub>N<sub>5.5</sub>O<sub>38</sub> (1657.28): K 1.18, Mn 3.32, Mo 52.10, N 5.99. Found: K 1.12, Mn 3.30, Mo 51.97, N 5.70.

Crystal structure of the title complex was determined by X-ray single crystal diffraction [15]. The title complex crystallizes in the trigonal system, space group R 32 with  $a = 15.846(4)$ ,  $c = 12.396(3)$  Å, and Mr = 1657.28. The heteropoly anion in the title compound has a novel Waugh structure (1:9) [16]. Nine MoO<sub>6</sub> octahedra are condensed by sharing oxygen atoms to form a [MnMo<sub>9</sub>O<sub>32</sub>]<sup>6-</sup> complex anion frame. Manganese (IV) atom is coordinated by six oxygen atoms from six MnO<sub>6</sub> octahedra, the MnO<sub>6</sub> octahedron being in the center of anion [MnMo<sub>9</sub>O<sub>32</sub>]<sup>6-</sup>.

The IR spectrum of the title compound is shown in Fig. 1. The  $\nu(\text{N-H})$  and  $\delta(\text{H-N-H})$  absorption bands in NH<sub>4</sub><sup>+</sup> group are located at 3159 and 1402 cm<sup>-1</sup>, respectively. The  $\nu(\text{O-H})$  and  $\delta(\text{H-O-H})$  of H<sub>3</sub>O<sup>+</sup> group appear at 3520 and 1612 cm<sup>-1</sup>, respectively. The strong and broad bands at 936 and 903 cm<sup>-1</sup> are assigned to  $\nu_{\text{Mo-O}}$  absorption vibration. The bands at 686, 591 and 543 cm<sup>-1</sup> are attributed to  $\delta_{\text{Mo-O-Mo}}$ . The absorption bands of  $\nu_{\text{Mn-O}}$  and  $\delta_{\text{Mn-O-Mo}}$  are possibly covered by  $\nu_{\text{Mo-O}}$  and  $\delta_{\text{Mo-O-Mo}}$  [13].

The thermal decomposition process of Mn(IV)Mo complex has been studied by means of differential thermal analysis (DTA) and thermogravimetric analysis (TG). Fig. 2 shows the curves of DTA and TG in N<sub>2</sub>. Two absorption peaks are found from 333 to 543 K, one (358.3 K) belongs to dehydration of absorption water, and the other (476.5 K) to dehydration of crystal water. The peaks at 579 and at 611K are attributed to the decomposition of ammonia. The complex loses 15.395% in weight from 283

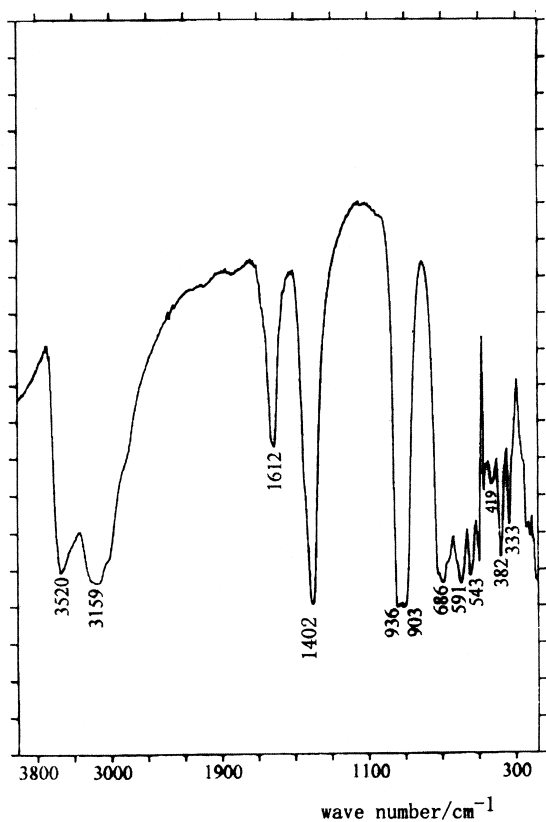


Fig. 1. IR spectrum of the title compound.

to 803 K, which is supposed to be due to the decomposition of the water and ammonia. The

data displayed in Fig. 2 shows that the  $[\text{MnMo}_9\text{O}_{32}]^{6-}$  has good thermal stability.

ESR spectrum data of the title complex solution at room temperature are as follows:  $g_1 = 4.1557$ ,  $g_2 = 3.4607$  and  $g_3 = 2.0428$ , which are assigned to Mn(IV). When  $\text{H}_2\text{O}_2$  was added into the title complex solution, the signal for Mn(IV) disappears while a superfine splitting peak with  $g = 1.9882$ ,  $\bar{A} = 94$  G appears, which is possibly attributed to  $\text{Mn}^{2+}$  (Fig. 3).

### 3.2. Catalytic hydroxylation

Activity of different catalysts in phenol hydroxylation is listed in Table 1. Based on the experimental data, the Mn(IV)Mo complex in the presence of  $\text{V}_2\text{O}_5$  has excellent catalytic activity for phenol hydroxylation.

### 3.3. The influence of Mn(IV)Mo complex and $\text{V}_2\text{O}_5$ content

Table 2 illustrates the effect of Mn(IV)Mo and  $\text{V}_2\text{O}_5$  content on phenol conversion and product distribution. In the early stage of the reaction, phenol conversion and HQ yield in-

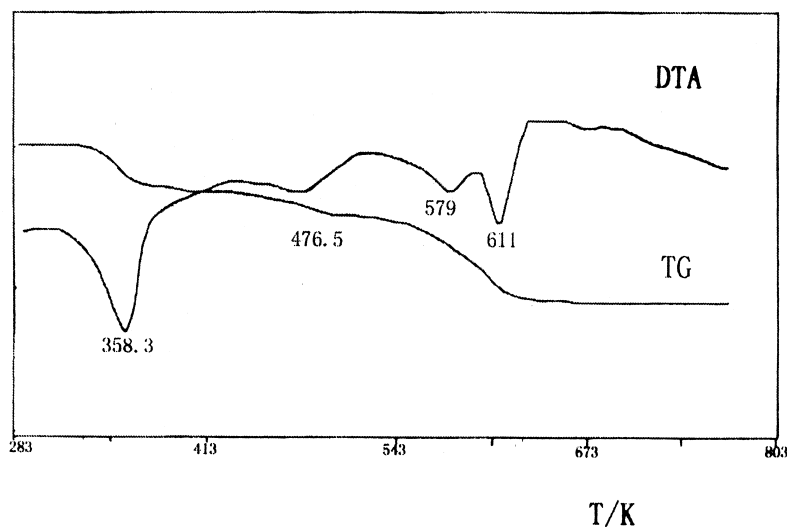


Fig. 2. DTA and TG curves of the title compound.

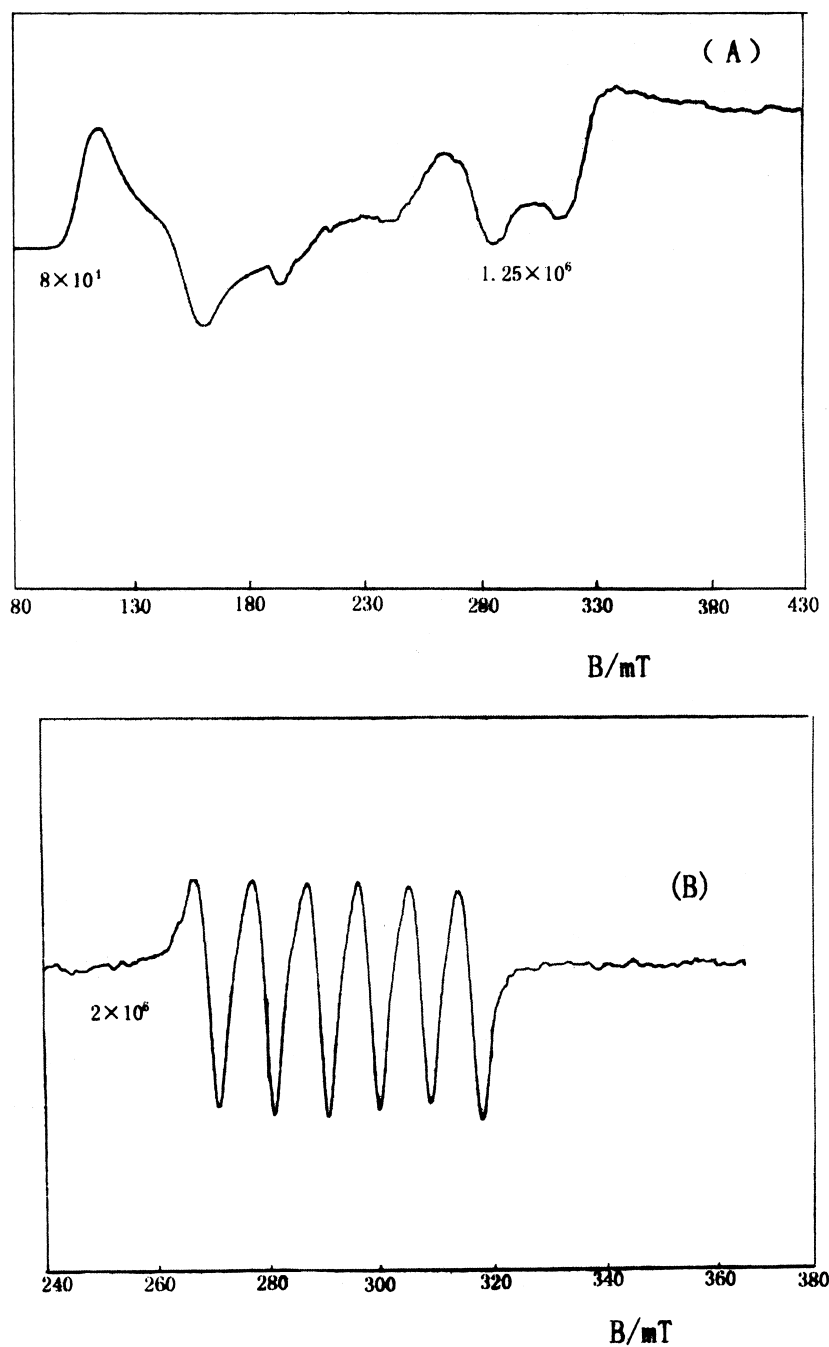


Fig. 3. (A) ESR spectrum of  $K_{0.5}(NH_4)_{5.5}[MnMo_9O_{32}] \cdot 6H_2O$ .  $g_1 = 4.1557$ ;  $g_2 = 3.4607$ ;  $g_3 = 2.0428$ . (B) ESR spectrum of  $K_{0.5}(NH_4)_{5.5}[MnMo_9O_{32}] \cdot 6H_2O + H_2O_2$ .  $g_1 = 1.9882$ ;  $A = 94$  G.

crease with Mn(IV)Mo and  $V_2O_5$  content, respectively. Both conversion of phenol and HQ yield reach the highest value when the added

amounts of Mn(IV)Mo and of  $V_2O_5$  reached up to 9.40 and 1.88 g/mol phenol, respectively. However, lower HQ yield and higher BQ yield

Table 1

Activity of different catalysts in phenol hydroxylation. HQ = hydroquinone, CAT = catechol, BQ = benzoquinone. Reaction time, 5 h; reaction temperature, 343 K; solvent, methanol; phenol:H<sub>2</sub>O<sub>2</sub> (molar ratio) = 1:1; mass of catalyst used: Mn(IV)Mo 50 mg, V<sub>2</sub>O<sub>5</sub> 10 mg

Catalyst	Phenol conversion (%)	Product distribution(%)		
		HQ	CAT	BQ
None	0	0	0	0
Mn(IV)Mo	10.73	9.46	0	0.27
Ammonium molybdate	0.12	0	0	0.02
V <sub>2</sub> O <sub>5</sub>	10.42	2.50	0	7.90
Ammonium molybdate + V <sub>2</sub> O <sub>5</sub>	13.74	13.20	0	0.20
Mn(IV)Mo + V <sub>2</sub> O <sub>5</sub>	45.04	38.64	0	2.09

are present beyond 9.40 g Mn(IV)Mo/mol phenol and 1.88g V<sub>2</sub>O<sub>5</sub>/mol phenol. Therefore, 9.40 g Mn(IV)Mo/mol phenol with 1.88g V<sub>2</sub>O<sub>5</sub>/mol phenol is a better selection for phenol hydroxylation, and the simultaneous action of suitable amounts of Mn(IV)Mo and V<sub>2</sub>O<sub>5</sub> can improve catalytic activity for phenol hydroxylation distinctively.

### 3.4. Influence of reaction time

The appropriate reaction time is the main assurance for the perfect reaction. Too long a time appears to be unfavorable for the phenol hydroxylation. Table 3 shows that the fit reaction time is 5 h. There was no significant change in the conversion and the product distribution beyond 5 h.

### 3.5. Influence of solvent

Solvent had distinct effects on the phenol hydroxylation. As listed in Table 4, the methanol is the best one for phenol hydroxylation in all reviewed solvents. In addition, the dioxane is the better one. The HQ yield is only 2.63% in acetone. There is almost no activity for phenol hydroxylation in water. The influence of solvent on the product distribution is more complex. The study of the two-phase reaction mechanism of heteropoly compound shows that the active species in the reaction system are produced in water phase, but the oxidation proceeds easily in the organic phase [17]. So selecting the suitable solvent is important for phenol hydroxylation. Methanol can dissolve both H<sub>2</sub>O<sub>2</sub> and phenol well, therefore, it is the most suitable

Table 2

The influence of K<sub>0.5</sub>(NH<sub>4</sub>)<sub>5.5</sub>(MnMo<sub>9</sub>O<sub>32</sub>) · 6H<sub>2</sub>O and V<sub>2</sub>O<sub>5</sub> content. Reaction time, 5 h; reaction temperature, 343 K; solvent, methanol; phenol:H<sub>2</sub>O<sub>2</sub> (molar ratio) = 1:1

Catalysts (g/mol pH OH)		Phenol conversion (%)	Product distribution (%)		
V <sub>2</sub> O <sub>5</sub>	Mn(IV)Mo		HQ	CAT	BQ
0	9.40	10.73	9.46	0	0.27
0.94	9.40	40.28	36.71	0	1.80
1.88	9.40	45.04	38.64	0	2.09
2.82	9.40	45.50	37.89	0	3.01
3.74	9.40	45.30	34.10	0	5.20
4.70	9.40	44.80	33.75	0	6.58
1.88	1.88	26.00	18.78	0	2.83
1.88	5.64	35.08	28.20	0	2.94
1.88	9.40	45.04	38.64	0	2.09
1.88	13.26	43.92	36.76	0	2.66
1.88	16.92	42.97	35.96	0	2.35

Table 3

The influence of reaction time. Reaction time, 5 h; reaction temperature, 343 K; solvent, methanol 15 ml; phenol:H<sub>2</sub>O<sub>2</sub> (molar ratio) = 1:1; mass of catalyst used: Mn(IV)Mo 50 mg, V<sub>2</sub>O<sub>5</sub> 10 mg

Reaction time (h)	Phenol conversion (%)	Product distribution (%)			Volume of O <sub>2</sub> evolved (ml)
		HQ	CAT	BQ	
1	22.13	19.81	0	0.24	25.00
2	35.54	30.03	0	0.85	28.00
3	37.81	31.61	0	2.18	32.00
4	40.57	34.20	0	2.30	30.15
5	45.04	38.64	0	2.09	34.20
6	45.90	38.46	0	2.54	29.73
7	46.01	38.54	0	2.44	35.00

Table 4

The influence of solvent. Reaction time, 5 h; reaction temperature, 343 K; phenol:H<sub>2</sub>O<sub>2</sub> (molar ratio) = 1:1; mass of catalyst used: Mn(IV)Mo 50 mg, V<sub>2</sub>O<sub>5</sub> 10 mg

Reaction time (h)	Phenol conversion (%)	Product distribution (%)			Volume of O <sub>2</sub> evolved (ml)
		HQ	CAT	BQ	
Acetone	2.63	2.63	0	0	69.20
Dioxane	18.24	16.20	0	2.00	20.24
Methanol	45.04	38.64	0	2.09	34.20
Water	0.80	0.80	0	0	35.34

Table 5

The influence of pH value. Reaction time, 5 h; reaction temperature, 343 K; solvent, methanol 15 ml; phenol:H<sub>2</sub>O<sub>2</sub> (molar ratio) = 1:1; mass of catalyst used: Mn(IV)Mo 50 mg, V<sub>2</sub>O<sub>5</sub> 10 mg

PH value	Phenol conversion (%)	Product distribution (%)			Volume of O <sub>2</sub> evolved (ml)
		HQ	CAT	BQ	
2	18.42	13.99	0	2.65	38.26
3	23.31	17.12	0	2.18	32.60
4	27.14	20.00	0	2.92	32.00
5	44.64	36.64	0	2.19	35.70
6	45.04	38.64	0	2.09	34.20
7	18.12	13.52	0	3.10	75.05
8	3.50	3.22	0	0.28	100.30
9	0.80	0.80	0	0	80.00
10	0	0	0	0	46.30

Table 6

The influence of reaction temperature. Reaction time, 5 h; solvent, methanol 15 ml; phenol:H<sub>2</sub>O<sub>2</sub> (molar ratio) = 1:1; mass of catalyst used: Mn(IV)Mo 50 mg, V<sub>2</sub>O<sub>5</sub> 10 mg

Reaction temperature (K)	Phenol conversion (%)	Product distribution (%)			Volume of O <sub>2</sub> evolved (ml)
		HQ	CAT	BQ	
313	12.41	5.18	0	3.20	12.00
323	23.52	17.03	0	3.89	28.00
333	41.44	34.51	0	2.75	29.44
343	45.04	38.64	0	2.09	34.20
353	46.81	38.67	0	3.33	38.60

Table 7

The influence of phenol/H<sub>2</sub>O<sub>2</sub> molar ratio. Reaction time, 5 h; reaction temperature, 343 K; solvent, methanol 15 ml; mass of catalyst used: Mn(IV)Mo 50 mg, V<sub>2</sub>O<sub>5</sub> 10 mg

Phenol/H <sub>2</sub> O <sub>2</sub> (molar ratio)	Phenol conversion (%)	Product distribution (%)			Volume of O <sub>2</sub> evolved (ml)
		HQ	CAT	BQ	
3:1	20.23	16.89	0	1.85	19.85
2:1	26.04	17.77	0	2.42	20.00
1:1	45.04	38.64	0	2.09	34.20
1:1.5	45.87	38.22	0	3.61	51.88
1:2	45.84	36.00	0	3.50	84.62
1:3	44.80	36.20	0	3.78	90.00

solvent for phenol hydroxylation when the title compound is used as catalyst.

### 3.6. Influence of pH value

Selecting methanol as the reaction medium, Mn(IV)Mo and V<sub>2</sub>O<sub>5</sub> as the catalyst and the promoter, respectively, Table 5 illustrates that the pH values of the reaction medium also has effects on phenol hydroxylation. Neither the strong acid nor basic environment is good for phenol hydroxylation, especially basic medium. There is almost no catalytic activity when pH = 10. The weak acidic medium is a better choice for phenol hydroxylation. (2 mol l<sup>-1</sup> sodium hydroxide and 2 mol l<sup>-1</sup> chlorhydric acid solution are used for pH adjustment in the reaction system.)

### 3.7. Influence of reaction temperature

Table 6 presents the effect of reaction temperature on hydroxylation of phenol. Below 343 K, both conversion of phenol and the yield of HQ increase with temperature. At 343 K, the HQ yield is the highest. Whereas, above 343 K, high temperature would lead to accelerating decomposition of H<sub>2</sub>O<sub>2</sub>, which is not beneficial to phenol hydroxylation. Hence, the suitable temperature is kept at 343 K.

### 3.8. Influence of phenol/H<sub>2</sub>O<sub>2</sub> molar ratio

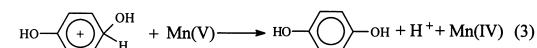
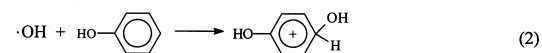
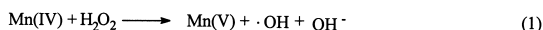
As shown in Table 7, the increase of the amount of H<sub>2</sub>O<sub>2</sub> can improve the phenol con-

version and HQ yield, and BQ yield as well. Probably the reason for BQ increase lies in the fact that excess H<sub>2</sub>O<sub>2</sub> may cause further oxidation of the HQ. Therefore, the phenol/H<sub>2</sub>O<sub>2</sub> molar ratio is best kept at 1:1 for phenol hydroxylation.

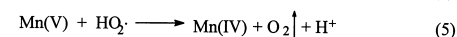
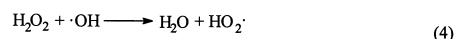
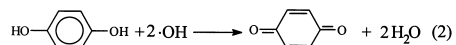
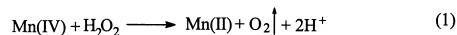
### 3.9. Mechanism of phenol hydroxylation

Many mechanisms of phenol hydroxylation have been put forward, such as free radical mechanism, peronium salt mechanism, etc. [2,19,20]. The study in the literature [18,21,22] indicates that the active species is ·OH in the hydroxylation of organic compound with H<sub>2</sub>O<sub>2</sub> as an oxygen donor. ·OH shows the characteris-

main reactions:



side reactions:



Scheme 1. Proposed mechanism for phenol hydroxylation.

tic of electrophilic substitution in the hydroxylation of aromatic ring. Our investigations have demonstrated that ammonium molybdate used as the sole catalyst has no catalytic activity in phenol hydroxylation. Meanwhile, they have low catalytic activity, if Mn(IV)Mo and V<sub>2</sub>O<sub>5</sub> are used as a catalyst, respectively. But the activity can be enhanced greatly when Mn(IV)Mo is used as catalyst, adding a small amount of V<sub>2</sub>O<sub>5</sub>. According to these results and ESR spectra analysis, Mn(IV) may possibly be regarded as a catalytic activity center and V(V) as catalyst promoter. Reaction mechanism for phenol hydroxylation catalyzed by Mn(IV)Mo may be proposed as Scheme 1. In the process of reaction H<sub>2</sub>O<sub>2</sub> can get one electron from Mn(IV)Mo to produce Mn(V)Mo and active species ·OH and OH<sup>-</sup>. Lack of ESR signal of Mn(V), as shown in Fig. 3, may arise because Mn(V)Mo is an unstable active intermediate. As soon as Mn(V)Mo is produced, main reaction (3) in the mechanism is likely to occur immediately. This is favorable for the production of hydroquinone. Yet, ESR signal of Mn(II) may be caused by side reaction (1).

Meanwhile, the above mechanism also shows that the decomposition of H<sub>2</sub>O<sub>2</sub> is a competitive reaction of phenol hydroxylation. But adjusting the pH value of the reaction system can effectively control the decomposition of H<sub>2</sub>O<sub>2</sub>. The catalytic activity increases greatly by adding a small amount of V<sub>2</sub>O<sub>5</sub>, it is probably because V<sub>2</sub>O<sub>5</sub> and H<sub>2</sub>O<sub>2</sub> can form the pervanadate which can react easily with phenol to form diphenol [2,19]. The concerted catalysis of suitable amounts of Mn(IV)Mo and V<sub>2</sub>O<sub>5</sub> lead to higher catalytic activity in phenol hydroxylation than any other reports now available.

## Acknowledgements

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