

# Hydroxylation of phenol with hydrogen peroxide over tungstovanadophosphates with Dawson structure

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## Abstract

Tungstovanadophosphates with Dawson structure (Cpyr)<sub>6+n</sub>P<sub>2</sub>W<sub>18-n</sub>V<sub>n</sub>O<sub>62</sub> ( $n = 1-3$ , Cpyr = Cetylpyridinium) were synthesized and characterized by IR and NMR. The hydroxylation of phenol with 30% aq. hydrogen peroxide was carried out using the catalysts. The results indicate that vanadium is the active substance in the reaction.

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**Keywords:** Tungstovanadophosphates; Dawson structure; Hydroxylation of phenol; Hydrogen peroxide; Dihydroxybenzenes

Dihydroxybenzenes (DHBs) are important chemicals; their production from hydroxylation of aromatic compounds is always of great interest to chemists, in particular for phenol direct hydroxylation [1]. It is said that the process of phenol hydroxylation with 30% aq. H<sub>2</sub>O<sub>2</sub> would be one of the most useful processes in the future [2] because of its simplicity and lack of pollution. Various catalysts, such as micro-porous TS and Ti-beta zeolites [1,3,4], simple metal ions [5], metal complexes [6,7], and polyoxometalates (POMs) [8–10], have been studied in the reaction of phenol hydroxylation. One of them, Takehira et al. [9,10], previously reported the hydroxylation of phenols with 30% aq. H<sub>2</sub>O<sub>2</sub> to produce DHBs using vanadium-containing POMs with Keggin structure.

The acid–base and redox behaviors of POMs play an important role in synthesis and applications, especially homogeneous and heterogeneous catalysis. The properties are dependent on the nature and the relative positions of the metals in the framework because the acid and redox properties of POMs can be controlled at the atomic and

molecular levels by changing the constituent elements. Molybdenum and tungsten are the main constitutive metals in POMs. For increasing the oxidizing ability, vanadium is usually substituted for molybdenum or tungsten to form the vanadium-substituted POMs, which are used for many oxidation reactions [11–13].

In the present work, vanadium-substituted POMs, tungstovanadophosphates with Dawson structure, H<sub>6+n</sub>P<sub>2</sub>W<sub>18-n</sub>V<sub>n</sub>O<sub>62</sub> ( $n = 1-3$ ) (P<sub>2</sub>W<sub>18-n</sub>V<sub>n</sub>), were synthesized and then transferred into their corresponding cetylpyridinium salts, (Cpyr)<sub>6+n</sub>P<sub>2</sub>W<sub>18-n</sub>V<sub>n</sub>O<sub>62</sub> ( $n = 1-3$ , Cpyr = Cetylpyridinium) (Cpyr-P<sub>2</sub>W<sub>18-n</sub>V<sub>n</sub>). The activity of phenol hydroxylation with 30% aq. H<sub>2</sub>O<sub>2</sub> to produce DHBs was then measured over these catalysts.

## 1. Experimental

The synthesis of tungstovanadophosphates with Dawson structure, P<sub>2</sub>W<sub>18-n</sub>V<sub>n</sub> ( $n = 1-3$ ), and their corresponding salts, Cypr-P<sub>2</sub>W<sub>18-n</sub>V<sub>n</sub> ( $n = 1-3$ ), has been previously reported [14,15].

Hydroxylation of phenol with 30% aq. H<sub>2</sub>O<sub>2</sub> was run in a 25 mL double layer glass reactor equipped with a reflux

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condenser, a magnetic stirrer, an air-tight gas measuring apparatus, and a superthermostat. Into the reactor, a measured amount of catalyst, 1.0 g of phenol and 10 mL of CH<sub>3</sub>CN were added, respectively. After the mixture was heated to the temperature desired, a measured amount of 30% aq. H<sub>2</sub>O<sub>2</sub> was added, and then the gas measuring apparatus was sealed. The volume of oxygen formed in the reaction was periodically recorded, based on its volume and the distribution of products, the selectivity of H<sub>2</sub>O<sub>2</sub> was calculated.

IR spectra were recorded on Nicolet 5DX FTIR spectrometer in KBr disks at room temperature. The solution for NMR measurements was obtained by dissolving the tungstovanadophosphates in acetonitrile. The spectra were recorded on Unity 400 NMR spectrometer. <sup>31</sup>P NMR chemical shifts were referenced to 85% H<sub>3</sub>PO<sub>4</sub> at the working frequency of 161.90 MHz.

The products were analyzed on gas chromatograph (Shimadzu 14B, temperature programmed, 70–200 °C, 2 °C/min, FID detector) with a Shimadzu fused silica capillary column (code: CBP1-M50-025). Shimadzu CR3A data processor was used for integrating. The calculation method agrees with that of [16].

## 2. Results and discussion

### 2.1. IR results

IR spectra of P<sub>2</sub>W<sub>18–n</sub>V<sub>n</sub> (*n* = 1–3) and their corresponding salts Cpyr-P<sub>2</sub>W<sub>18–n</sub>V<sub>n</sub> (*n* = 1–3, Cpyr = Cetylpyridinium) presented in Fig. 1 strongly indicate that

the compounds have the same structures as α-P<sub>2</sub>W<sub>18</sub>. The characteristic peaks, 1078, 1013, 996, 884 cm<sup>-1</sup>, appeared at 800–1100 cm<sup>-1</sup> which can be assigned to the tungstovanadophosphates with Dawson structure [14], and the structures of corresponding salt Cpyr-P<sub>2</sub>W<sub>18–n</sub>V<sub>n</sub> (*n* = 1–3) are unchanged after the cetylpyridinium salts are formed.

### 2.2. NMR results

<sup>31</sup>P NMR chemical shifts data of the tungstovanadophosphates are presented in Table 1. For α-isomer of P<sub>2</sub>W<sub>18</sub> with Dawson structure, only one <sup>31</sup>P NMR signal is present at –12.44 ppm, but once tungsten atoms are substituted by vanadium atoms, the micro-environment of the two phosphorus atoms in the structure of P<sub>2</sub>W<sub>18–n</sub>V<sub>n</sub> (*n* = 1–3) will be different and two <sup>31</sup>P NMR signals will be

Table 1  
<sup>31</sup>P NMR data for Dawson tungstovanadophosphates

Anion	–δ/P(1)	–δ/P(2)
α-[P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> ] <sup>6–</sup>	12.44 <sup>a</sup>	12.44 <sup>a</sup>
[P <sub>2</sub> W <sub>17</sub> VO <sub>62</sub> ] <sup>7–</sup>	10.63(10.67) <sup>b</sup>	12.73
	10.84 <sup>a</sup>	12.92 <sup>a</sup>
[P <sub>2</sub> W <sub>16</sub> V <sub>2</sub> O <sub>62</sub> ] <sup>8–</sup>	8.56(8.61) <sup>b</sup>	13.17
	8.82 <sup>a</sup>	13.44 <sup>a</sup>
[P <sub>2</sub> W <sub>15</sub> V <sub>3</sub> O <sub>62</sub> ] <sup>9–</sup>	6.07(6.09) <sup>b</sup>	13.53
	6.25 <sup>a</sup>	13.90 <sup>a</sup>

<sup>a</sup> Ref. [9].

<sup>b</sup> The values in parantheses are calculated with Eq. (1) given in the text.

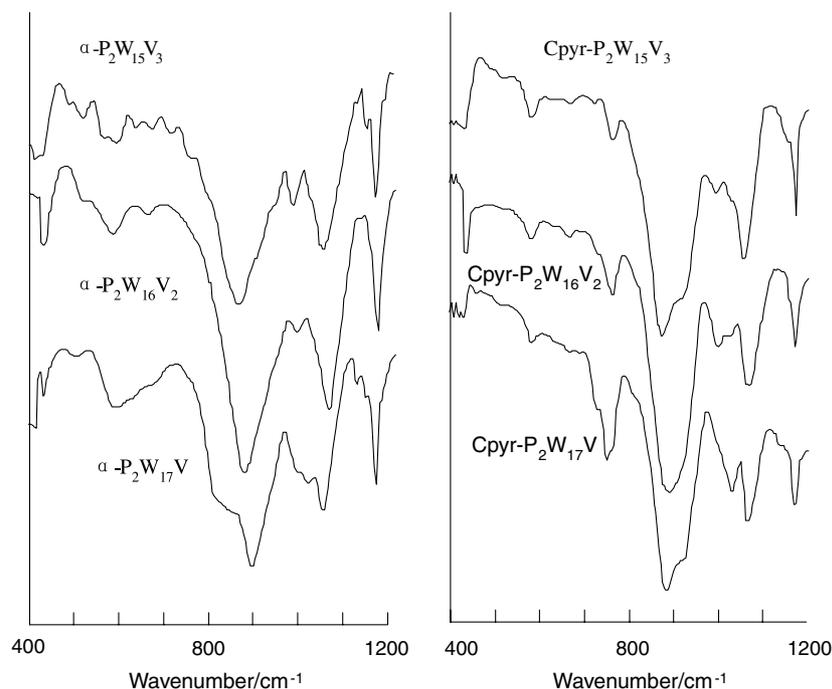


Fig. 1. IR spectra of Dawson tungstovanadophosphates.

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