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Catalytic wet peroxide oxidation of phenol by $[C_{16}H_{33}(CH_3)_3N]_4H_2SiV_2W_{10}O_{40}$ catalystHuacheng Li^a, Xia Yu^c, Hongwei Zheng^a, Yiming Li^a, Xiaohong Wang^{a,*}, and Mingxi Huo^{b,*}^a Key Lab of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast

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E-mail address: wangxh665@nenu.edu.cn**Abstract**

A micellar tungstovanadosilicic polyoxometalate (POM) catalyst $[C_{16}H_{33}(CH_3)_3N]_4H_2SiV_2W_{10}O_{40}$ (abbreviated as $[C_{16}]_4H_2SiV_2W_{10}$) was prepared and used for catalytic wet peroxide oxidation (CWPO) of phenol. Energy Dispersive X-Ray Spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), and ²⁹Si MAS NMR were used to characterize the resulting sample. The best catalytic activity was obtained by $[C_{16}]_4H_2SiV_2W_{10}$ with 91.6% degradation effect, 93.2% COD removal and 85.5% TOC reduction with H₂O₂ under room condition towards complete degradation product CO₂ within 90 min. The leaching test showed that the POM micellar catalysts had an excellent stability and can be used as heterogeneous catalysts for about six times.

Keywords: Catalytic wet peroxide oxidation, polyoxometalate, degradation, phenol**1. Introduction**

Catalytic wet oxidation of pollutants is a more promising process for wastewater treatment, where air, ozone, and hydrogen peroxide can be used as oxidants¹. Among oxidation processes, the hydrogen peroxide system containing a catalyst (Catalytic Wet Peroxide Oxidation, CWPO) has emerged as a clean and effective alternative²⁻⁶ due to no formation of harmful by-products,

non-toxic reactant, mild degradation conditions (20 ~ 80°C, atmospheric pressure), highly oxidative efficiency. By now, there are some reports on CWPO of phenol using H₂O₂/catalyst, Fenton like system, photo-Fenton, which are very efficient for the degradation of phenol. However, there are three major drawbacks including narrow acidic pH range (usually around 3.0), the need for removing of homogeneous catalysts, and low utilization of hydrogen peroxide, which result in the limitation for application. Compared to homogeneous one, heterogeneous catalysis appears as a promising alternative to overcome the above problems since oxidation efficiency is relatively higher and the pH sensitivity is lower under the same reaction conditions. Therefore, a variety of catalysts containing transition metals including Fe, Cu, Co, Cr, Mn, Ni supported on different materials (such as oxides, pillared clays, zeolites, activated carbon, natural and synthetic polymers) have been tested in CWPO ⁷⁻⁹ recent years. Up to now, the best efficiency catalyzed by Al-Fe pillared clays (5g/L) was obtained with 100% degradation of phenol (5×10^{-4} mol/L) and ~ 80% TOC removal at room temperature for 240 min. However, the operating pH needed to be controlled at 3.7 ¹⁰. Meanwhile, copper loaded catalyst CuO/ γ -Al₂O₃ gave complete phenol conversion and 85% TOC reduction with high peroxide efficiency close to stoichiometry ³ under 343 K for 3 h. However, leaching of copper from the support occurred, and needed to be solved further.

Polyoxometalates (POMs) are oxo-cluster of transition metals in their highest oxidation states, namely W (VI), Mo (VI) or V (V). They have been proved to be one of most efficient and widely used oxidative catalysts with hydrogen peroxide or oxygen as oxidants. N. Mizuno had reviewed that multi- transition metal-substituted POMs showed various functionalities such as cooperative activation of oxidants H₂O₂ or O₂, simultaneous activation of oxidants and substrates, stabilization of reaction intermediates, and multielectron transfer, leading to the remarkable activities and selectivities in comparison with conventional monometallic complexes ¹¹. And some POMs including H₃PW₁₂O₄₀ ¹², [SiW₁₀Fe₂O₃₈]⁶⁻ ¹³ or [n-Bu₄N]₃H₃[PW₉V₃O₄₀] ¹⁴ could act as oxidative catalysts using H₂O₂ as a oxidant involving a radical mechanism. During our research work, we found that vanadium-based polyoxometalates [(C_nH_{2n+1})N(CH₃)₃]_{3+x}PV_xMo_{12-x}O₄₀ could oxidize phenol using O₂ as a oxidant via a radical oxidative process ¹⁵. In the present paper, we report on an extension of our research work. We design a micellar POM [C₁₆]₄H₂SiV₂W₁₀ for CWPO of phenol. By now, [γ -SiW₁₀O₃₆V₂(μ -OH)₂]⁴⁻ had been reported as an excellent catalyst for selective

oxidation of hydrocarbons with H_2O_2 involving electrophilic oxidant-mediated mechanism¹⁶⁻¹⁸. To the best of our knowledge, there is no report on $[\gamma\text{-SiW}_{10}\text{O}_{36}\text{V}_2(\mu\text{-OH})_2]^{4-}$ in the oxidative degradation of pollutions in CWPO process.

Herein four main innovations are proposed. (1) The micellar POM catalyst $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$ could activate hydrogen peroxide via a radical mechanism. (2) The first example of highly efficient CWPO degradation of phenol under extremely mild condition in the micellar POM system. (3) The best result in CWPO of phenol within short time, which is not limited by the pH of the reaction. (4) The leaching test showed that $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$ has an excellent stability and can be reused as a rapid heterogeneous catalyst for about six times by simply treatment, which solves the separated problem.

2. Experimental

2.1 Materials

All reagents were of AR grade and used without further purification. 0.53mM solution of phenol was prepared. $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$ were prepared according to Ref¹⁹, and were characterized by IR spectroscopy and ^{29}Si MAS NMR.

2.2 Physical measurement

Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400 CHN elemental analyzer. FT-IR spectra ($4000\text{--}400\text{cm}^{-1}$) were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. ^{29}Si MAS NMR spectra of catalysts were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CPMAS probehead. TEM image was measured on JOEL JEM-2100F microscope. Analysis of phenol and intermediates during the reaction was performed by high pressure liquid chromatogram (HPLC, Shimadzu LC-20A) with a UV detector using a Shim-pack VP-ODS (4.6mm \times 250mm, 5 μm) column. The mobile phase was a mixture of 50% water, and 50% methanol with a flow rate of 0.5mL/min. Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400 CHN elemental analyzer. A DX-300 ion chromatograph (IC) equipped with a conductivity detector and an ICE-ASI anion column was also used to determine the changes of the concentrations of the intermediates and final product.

2.3 Preparation of $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$

$\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$ (0.8g, 2.7mmol) was dissolved in 2.8mL of HCl (1M) aqueous solution.

NaVO_3 (1.1 mL, 0.5M) aqueous solution was added into the above solution with gently stirring for 10min, then the dark red solution was filtered. 0.8g (2.5mmol) of hexdecyltrimethylammonium bromide (CTAB) was added to the filtrate. The pale yellow precipitate formed immediately and was collected by filtration. The solid was recrystallized by acetonitrile for two times, then it was calcinated at 100 °C for about 3h with yield of 68%.

2.4 Critical micelle concentration (CMC) determination

The CMC of $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$ was determined at break points of two line portions of the specific conductivity versus concentration plot²⁰.

2.5 Cyclic voltammetry experiments

Cyclic voltammetry was conducted in a CHI600 voltammetric analyzer with a three compartment cell at ambient temperature (25 ± 1 °C). A commercial Ag/AgCl electrode was used as the reference electrode, a platinum wire as the counter electrode and a glass carbon electrode (GCE) as the working electrode. The GCEs were polished with 1.0 and $0.3\mu\text{m}$ α - Al_2O_3 powders, and sonicated in deionized water for 10min. Finally, the electrodes were sonicated in ethanol, washed, and then dried in a high purity nitrogen steam before use.

2.6 Catalytic procedure

A typical catalytic reaction was carried out as follows: 150 mg of catalyst was suspended in a fresh aqueous phenol solution ($C_0 = 0.53\text{mM}$, 50mL, pH = 2.83) in a 100mL three-neck flask at ambient temperature. Then the oxidation reaction was activated by addition certain amount of hydrogen peroxide (30 wt%). In order to confirm the high utility of H_2O_2 , the hydrogen peroxide was added intermittently other than the whole amount at one time. Furthermore, the H_2O_2 addition interval depends on the length of experiment, usually at a rate of 0.2 mL/15min when 90 min reaction time and 1.2 mL hydrogen peroxide was required. Then liquid sample was taken at different time and was immediately detected the degradation of phenol by a 4-Aminoantipyrine spectrophotometric method²¹ and high performance liquid chromatogram (HPLC). The utility of H_2O_2 was detected by the titration method with $\text{Ce}(\text{SO}_4)_2$ ²². When the reaction finished, the catalyst was separated by centrifuge in 2500 rpm for 2 min and washed with water for three times to be reused.

2.7 TOC and COD determinations

10mL liquid sample was taken at different time and then immediately detected and measured by

a Total Organic Carbon Analyzer (Shimadzu TOC-VCPN). Then 10 mL distilled water sample was processed in the same way as blank test.

$$\text{TOC removal efficiency (\%)} = \frac{(T_i - T_0) - (T_f - T_0)}{(T_i - T_0)} \times 100\%$$

T_i : the initial TOC in liquid sample.

T_f : the final TOC in liquid sample.

T_0 : the TOC in blank test.

10 mL liquid sample was taken at different time and then detected by the conventional dichromate method (COD_{Cr}). Then 10 mL distilled water sample was processed in the same way as blank test.

$$\text{COD}_{\text{Cr}} \text{ removal efficiency (\%)} = \frac{(C_i - C_0) - (C_f - C_0)}{(C_i - C_0)} \times 100\%$$

C_i : the initial COD in liquid sample.

C_f : the final COD in liquid sample.

C_0 : the COD in blank test.

2.8 Radical' scavenging test

The test was conducted as follows: 2 mM of scavenging agent was added into a fresh aqueous phenol solution ($C_0 = 0.53$ mM, 50mL, pH = 2.83) with catalyst (0.80 mM) and H_2O_2 (0.23 M) in a 100mL three-neck flask at ambient temperature for 90 min. The final concentration of phenol was detected by the same method.

3. Results and discussion

3.1 Characterization

From the results of the elemental analyses, the C, H, N, W, Si and V contents in $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$ are C, 23.32; H, 4.46; N, 1.54; Si, 0.80; W, 49.06; and V, 2.84%, respectively. Compared to the calculated values C, 24.35; H, 4.57; N, 1.54; Si, 0.75; W, 49.05; and V, 2.72%, the results are satisfactory.

The IR spectra of $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$ and $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}] \cdot 12\text{H}_2\text{O}$ were investigated (Fig. 1). Peaks at 952 (vas $\text{W}=\text{O}_d$), 916 (vas $\text{Si}-\text{O}_a$), and 786 cm^{-1} (vas $\text{W}-\text{O}_c-\text{W}$), respectively, indicated that $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$ maintained the Keggin structure. Compared to $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}] \cdot 12\text{H}_2\text{O}$ (989 (vas $\text{W}=\text{O}_d$), 944 (vas $\text{Si}-\text{O}_a$), 866 (vas $\text{W}-\text{O}_b-\text{W}$), and 791 cm^{-1} (vas $\text{W}-\text{O}_c-\text{W}$), respectively),

there were some shifts indicating the vanadium incorporation into vacancy of $\text{SiW}_{10}\text{O}_{36}^{8-}$. In addition, the peaks at 2922, 2852, and 1468 cm^{-1} were attributed to C–H, and C–N, respectively, showing the existence of quaternary ammonium in $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$.

Fig. 1

^{29}Si MAS NMR spectrum was recorded for $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$ (Fig. 2). It can be seen that one signal peak at -91 ppm, indicating that $\text{SiV}_2\text{W}_{10}\text{O}_{40}^{6-}$ remained intact upon assembly of quaternary ammonium cation and POM anion.

Fig. 2

The morphology of $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$ was examined by TEM (Fig. 3). From our previous report²³, it is known that the POM amphiphile molecules could form micellar assembly in water with nanospheric structure. The TEM image of $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$ demonstrated the formation of micelles in water with nanosize around 2 nm. The result of EDX gave each element contents as: V, 2.94; Si, 0.78; W, 49.89; C, 23.32 and N, 1.57%, which were consistent with the elementary results. The result of the critical micelle concentration (CMC) also determined the formation of micelles. The plot of the specific conductivity versus the concentration of $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$ showed a break point of nearly two straight line portions giving the CMC as 8.0×10^{-4} mol/L (Fig. S1).

Fig. 3

The electrochemical behavior of $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$ had been studied by CV^{24,25}. As shown in Fig. 4, the $\text{SiV}_2\text{W}_{10}\text{O}_{40}^{6-}$ exhibits five redox waves in the potential range 0.4V to -0.7V. They are assigned to a one-electron vanadium-centered (waves I: $\text{V}^{\text{V}} \rightarrow \text{V}^{\text{IV}}$), a one-electron tungsten-centered (waves II: $\text{W}^{\text{VI}} \rightarrow \text{W}^{\text{V}}$), a two-electron vanadium-centered (waves III: $\text{V}^{\text{V}} \rightarrow \text{V}^{\text{III}}$), a one-electron tungsten-centered (waves IV: $\text{W}^{\text{VI}} \rightarrow \text{W}^{\text{V}}$) and a two-electron tungsten-centered (waves V: $\text{W}^{\text{VI}} \rightarrow \text{W}^{\text{IV}}$).

Fig. 4

3.2 The catalytic activity of $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$

A preliminary experiment was performed at 25°C and atmospheric pressure in the existence of hydrogen peroxide without any no catalyst or with different catalysts including CTAB, $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$, and $\text{K}_4\text{H}_2\text{SiV}_2\text{W}_{10}$ (Fig. 5). Without catalyst, the oxidation of phenol was negligible (less than 7%), showing that the oxidative ability of H_2O_2 was weak. In presence of

CTAB, the phenol disappearance increased at first 30 min, and then tented to equilibrium. This might be attributed to the adsorption of phenol by CTAB. A large increase in phenol degradation was observed catalyzed by $K_4H_2[\gamma-SiV_2W_{10}O_{40}]$ with the degradation efficiency of 53.5 %. Under our reaction conditions, $K_4H_2[\gamma-SiV_2W_{10}O_{40}]$ was less soluble in water and formed heterogeneous system in degradation of phenol. Then, Fig. 5 highlighted the efficiency of $[C_{16}]_4H_2SiV_2W_{10}$ in such oxidation of phenol by H_2O_2 . As we observed before¹⁴, the phenol molecules could be concentrated on micellar POM catalyst, hence promoted the reaction rate. Therefore, the high activity of $[C_{16}]_4H_2SiV_2W_{10}$ was firstly attributed to phenol accumulation on the part of $SiV_2W_{10}O_{40}^{6-}$.

Fig. 5

At practical, high concentration of phenol is difficult to be solved. Therefore, the influence of phenol concentration is more important for the application in CWPO process. The experiments were conducted using different concentrations (0.15, 0.23, 0.31, 0.40, 0.53, 0.58, and 0.64 mM), while other variables were kept constants (Fig. 6). It can be seen that the phenol concentration has a great influence on its degradation. In the same usages of catalyst and H_2O_2 , increasing of phenol concentration could decrease the degradation efficiency. It was attributed to the limitation of catalytically active sites, which hindered the further adsorption of phenol resulting in lower activity. The phenol molecules being adsorbed by catalyst became saturate as its concentration of 0.53 mM. Therefore, the concentration of phenol was used as 0.53 mM during the whole reaction.

Fig. 6

The influence of pH (initial phenol solution adjusted with 1M HCl) on the degradation of phenol is well important for alternative CWPO process and is of great value for the operation in a wide range of pH (Fig. 7). Fig. 7 showed the degradation efficiency of phenol over $[C_{16}]_4H_2SiV_2W_{10}$ at pH values of 2.1, 2.8, 3.5, 4.2, 4.9, 5.6, 6.3 and 7.0. It can be seen that the pH of the reaction influenced the degradation of phenol. The maximum degradation efficiency was obtained at pH 2.8 with 91.6%. With the increase of pH, the degradation of phenol decreased. This might be attributed to the charge change of phenol. Increasing in pH led to the ionization of phenol to form $Ph-O^-$. Because the surface charges of POMs are negative, phenol molecules were repelled far away from catalytic centers resulting in a decrease in phenol adsorption onto the catalyst and a decrease in degradation efficiency. The UV-vis spectrum of the catalyst with

hydrogen peroxide in different pH could confirm its stability. (Fig. S2)

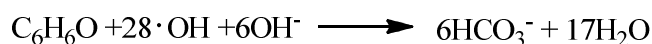
Fig. 7

The influence of usage of $[C_{16}]_4H_2SiV_2W_{10}$ on phenol degradation was studied and the results were shown in Fig. 8. The degradation efficiency showed an increasing trend as the concentration of $[C_{16}]_4H_2SiV_2W_{10}$ increased from 0 mM to 0.96 mM. A plateau appeared when the $[C_{16}]_4H_2SiV_2W_{10}$ concentration exceeded the CMC of 8.0×10^{-4} mol/L. This phenomenon is in agreement with bimolecular reactions³. By further increasing the concentration of catalyst to 0.96 mM, only a slight increase in the phenol degradation can be detected. 0.80 mM was an optimum concentration for the CWPO of phenol.

Fig. 8

The influence of hydrogen peroxide concentrations on the degradation of phenol had been studied (Fig. 9). The hydrogen peroxide concentration is related to the number of hydroxyl radicals generated in the oxidation process²⁶.

The stoichiometry for the degradation of phenol can be written as following:



In theory, 14 mol of H_2O_2 is needed to oxidize 1 mol of phenol. However, the optimal hydrogen peroxide concentration is 0.23 M in our experiment. Further increasing of H_2O_2 usage did not result in higher degradation efficiency due to the decomposition of H_2O_2 . The final molar ratio of H_2O_2 to phenol is about 230 corresponding to the stoichiometric value. To the best of our knowledge, the highest ratio of H_2O_2 to phenol was reported by now under room conditions.

Fig. 9

As previous reports, the CPWO of phenol underwent a radical mechanism. Firstly, we measured the radical formation in such CPWO process. The formation of possible oxidative intermediate species, such as singlet oxygen (1O_2), superoxide ($O_2^{\cdot-}$), and hydroperoxy (HO_2^{\cdot}), or (OH^{\cdot}), under CWPO conditions was investigated indirectly with the use of appropriate quenchers for these species. In this type of experiment, a comparison was made between the original degradation curves of phenol/ $[C_{16}]_4H_2SiV_2W_{10}$ dispersions and those obtained after the addition of millimolar concentrations of quenchers in the initial solution under otherwise identical conditions (Fig. S3). It can be seen that KI affected the degradation rate of phenol, indicating that the main active

oxidative species involved in this CWPO system is $\text{OH}\cdot$ ²⁷. Then NaN_3 and p-benzoquinone showed less influence on the degradation of phenol, indicating that single oxygen $^1\text{O}_2$ and $\text{O}_2\cdot^-$ might form as a possible oxidative intermediate species during the reaction²⁸⁻²⁹. These results demonstrated that the reaction took place mainly through an $\text{OH}\cdot$ radical mechanism.

The H_2O_2 decomposition experiments in absence of catalyst could demonstrate this phenomenon. Fig. S4 gave the decomposition efficiency of hydrogen peroxide in the presence of the catalyst and phenol, only substrate, and only catalyst.

According to Ma's study³⁰ and our results, the decomposition of H_2O_2 with POMs and phenol included two steps: zero-order reaction and first-order reaction. For the zero-order reaction at a given temperature, the rate equation is $C_0 - C_t = kt$, while the first-order rate equation is $\ln C_0 - \ln C_t = k' t$.

In the degradation of phenol by $[\text{C}_{16}]_4\text{H}_2\text{SiV}_2\text{W}_{10}$ with the H_2O_2

$$k_1 = (0.23 - 0.225) / 15 = 0.0003 \text{ mol} \cdot \text{min}^{-1} \cdot \text{L}^{-1}$$

$$k_2 (15-30 \text{ min}) = (\ln 0.225 - \ln 0.180) / 15 = 0.00817 \text{ min}^{-1}$$

$$k_3 (30-45 \text{ min}) = (\ln 0.180 - \ln 0.155) / 15 = 0.00877 \text{ min}^{-1}$$

$$k_4 (45-60 \text{ min}) = (\ln 0.155 - \ln 0.143) / 15 = 0.00537 \text{ min}^{-1}$$

k_2 , k_3 and k_4 were at the same order of magnitude, therefore, the reaction followed zero-order one at the first 15 min, while it underwent the first-order reaction from 15 to 60 min.

Meanwhile, we can assume that the activation energy (E_a) of the first-order reaction ranges from 43.26 kJ/mol (10.3 kcal/mol) to 115.08 kJ/mol (27.4 kcal/mol) referring to Ma's study³⁰, which corresponded well with the H_2O_2 activation energy 49.3 kJ/mol in N. S. Inchaurredo's report³. We use the 43.26 kJ/mol as the lowest activation energy for H_2O_2 decomposition. In

Arrhenius equation, $\ln \frac{k_5}{k_4} = -\frac{E_a}{R} \left(\frac{1}{T_5} - \frac{1}{T_4} \right)$, assuming $T_4 = 298\text{K}$, $T_5 = 343\text{K}$, $k_4 = 0.00537$

min^{-1} , we calculated $k_5 = 0.0531 \text{ min}^{-1}$, which had the same order of magnitude with N. S. Inchaurredo's report (0.0364 min^{-1} at 343K). The difference may be caused by using different catalytic metal center of V^{5+} and Cu^{2+} .

Our experiment was carried at room temperature (298K), so the temperature had a significant impact on the decomposition of H_2O_2 and rate coefficients (k). In the 343K, low concentration

hydrogen peroxide could just generate a large amount of $\text{OH}\cdot$, while in the 298K, as the rate coefficients decreased 9.7 to 443 times. In order to generate the same amount of $\text{OH}\cdot$, concentration of H_2O_2 needed to rise 9.7 to 443 times. The molar ratio of H_2O_2 to phenol was 433 in our CWPO process, which was within the range of 9.7 to 443.

3.3 The formation of peroxo-polyoxometalate during the CPWO process

During the CWPO, we assumed that the vanadium in the POM could interact with hydrogen peroxide to form an active intermediate of peroxovanadate. The Uv-vis spectrum of the reaction mixture could confirm this hypothesis (Fig. S5), which gave a weak band at 460 nm corresponding to $\eta^2\text{-O}_2\rightarrow\text{V}^{31}$. Meanwhile, the Keggin structure of $[\text{C}_{16}]_4\text{H}_2\text{SiW}_{10}\text{V}_2$ had been kept during the reaction, showing that POMs was stable under such reaction conditions.

3.4 Mineralization

To evaluate the oxidation degree of $[\text{C}_{16}]_4\text{H}_2\text{SiW}_{10}\text{V}_2$ towards phenol, the mineralization was investigated by monitoring TOC and COD changes. The COD reflects the extent of contamination by the reductive substances in water. The TOC reductions and the COD removal efficiencies of phenol catalyzed by $[\text{C}_{16}]_4\text{H}_2\text{SiW}_{10}\text{V}_2$ are 85.47% and 93.2%, respectively, at 90 min. As shown in Fig. 10 and Fig. 11, the degradation of phenol did not happen without $[\text{C}_{16}]_4\text{H}_2\text{SiW}_{10}\text{V}_2$, while with $[\text{C}_{16}]_4\text{H}_2\text{SiW}_{10}\text{V}_2$, phenol decreased from 2.62mg/L to 0mg/L within 30min, and the catechol decreased from 0.43mg/L to 0mg/L within 15min. There were no intermediates detected in the reaction process, indicating that the phenol might be oxidized to CO_2 and H_2O .

Fig. 10

Fig. 11

These results showed that phenol was totally mineralized in the above POM CWPO process.

3.5 Stability of catalyst

The stability of catalyst is more important property in heterogeneous CWPO process. After the experiment, the catalyst was collected by centrifuge in 2500rpm for 2 min and washed with water for three times to be reused. The regenerated reagent is as reactive as the freshly prepared catalyst. Based on IR (Fig. 1c) and ^{29}Si NMR (Fig. 2b) analysis, the catalyst structure does not change after six repeated experiments. The catalytic activity of phenol degradation is maintained efficiently after six repeated experiments, showing only a slight decrease in activity (Fig. 12). Moreover, the total amount of $[\text{C}_{16}]_4\text{H}_2\text{SiW}_{10}\text{V}_2$ leaching through six runs of the reaction reaches only 8.3% of

the starting amount.

Fig. 12

4. Conclusion

In this study, POM micellar catalyst $[C_{16}]_4H_2SiW_{10}V_2$ has been synthesized and used as catalysts in the CWPO of phenol under room condition. This micellar POM catalyst exhibited high efficiency in activation of H_2O_2 to degrade phenol under room temperature and atmospheric pressure within short time. The high performance of the catalyst was attributed to the micellar structure and the catalytic center $H_2SiV_2W_{10}O_{40}^{4-}$. More importantly, this CWPO process could deal with high concentration of phenol at a wide range of pH from 2 to 7. The catalyst exhibited consistent activity during recycling. Therefore, CWPO based on POM micellar catalyst is of great value for green chemistry and is potential for CWPO of phenol.

Acknowledgements

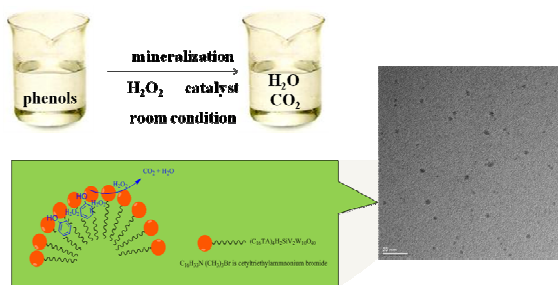
The authors are grateful for the financial supported by the National Natural Science Foundation of China (51078066 and 20871026), the foundation of Jilin Provincial Environmental Protection Bureau (No. 200929). This work was supported by the National College Students' Innovative Training Program (No. 201210200072).

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Under ambient temperature and atmospheric pressure condition, phenol could be completely oxidized to CO₂ with catalyst [C₁₆H₃₃(CH₃)₃N]₄H₂SiV₂W₁₀O₄₀.

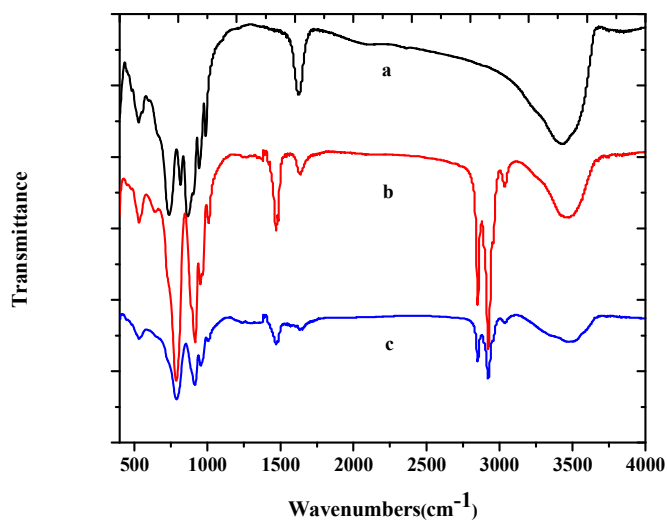


Fig. 1. The IR spectra of (a) $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}] \cdot 12\text{H}_2\text{O}$, (b) $[\text{C}_{16}]_4\text{H}_2\text{SiW}_{10}\text{V}_2$, and (c) $[\text{C}_{16}]_4\text{H}_2\text{SiW}_{10}\text{V}_2$ after six times cycling runs.

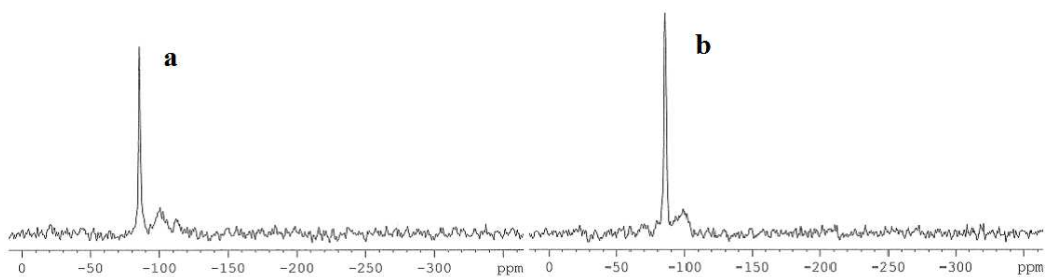


Fig. 2. The ²⁹Si NMR spectra of (a) $[\text{C}_{16}]_4\text{H}_2\text{SiW}_{10}\text{V}_2$, and (b) $[\text{C}_{16}]_4\text{H}_2\text{SiW}_{10}\text{V}_2$ after six times cycling runs

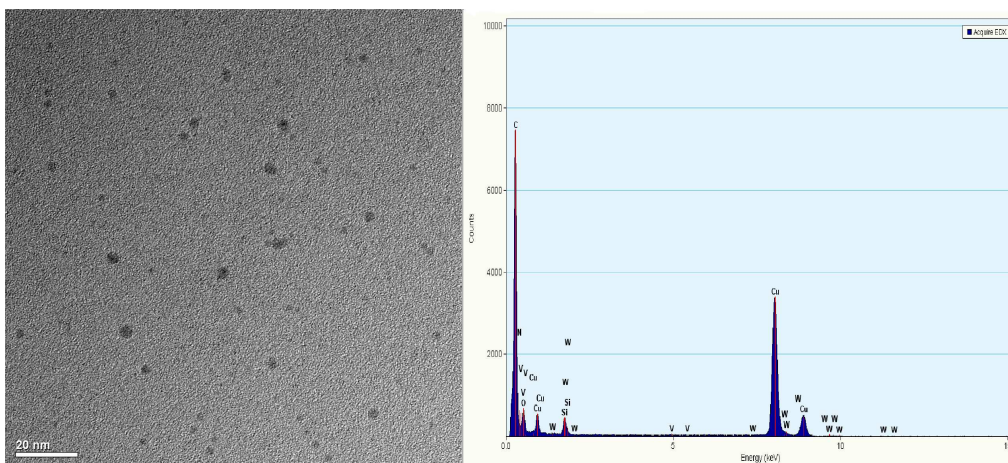


Fig. 3. The cryo-TEM image and EDX spectrum of $[\text{C}_{16}]_4\text{H}_2\text{SiW}_{10}\text{V}_2$ micellar catalyst.

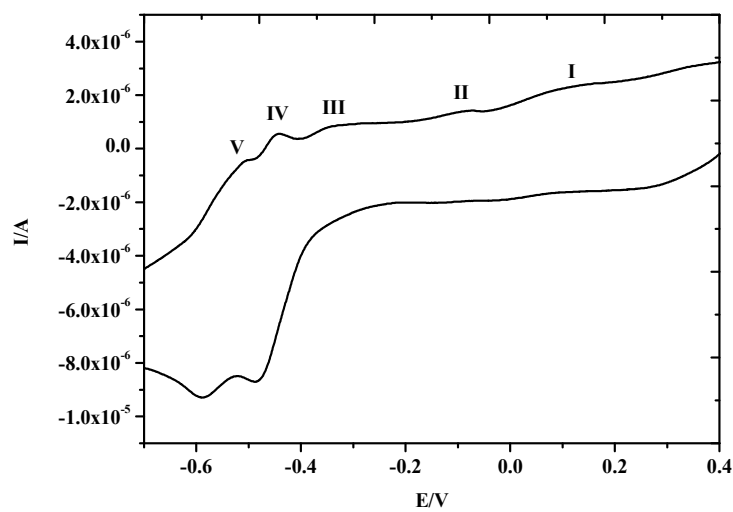


Fig. 4. CV of 1.225×10^{-3} mM $\text{K}_4\text{H}_2[\gamma\text{-SiV}_2\text{W}_{10}\text{O}_{40}]$ at pH = 2.1 ($\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4$)

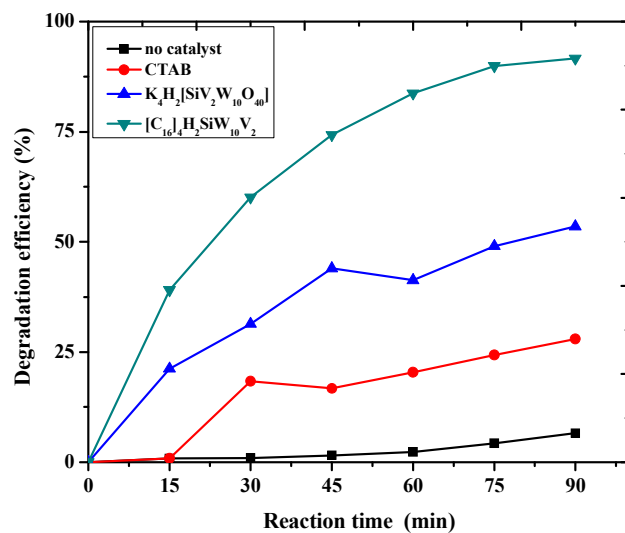


Fig. 5. The degradation efficiency of phenol (0.53mM) on different catalysts (0.80mM) with the hydrogen peroxide (0.23M) for different time

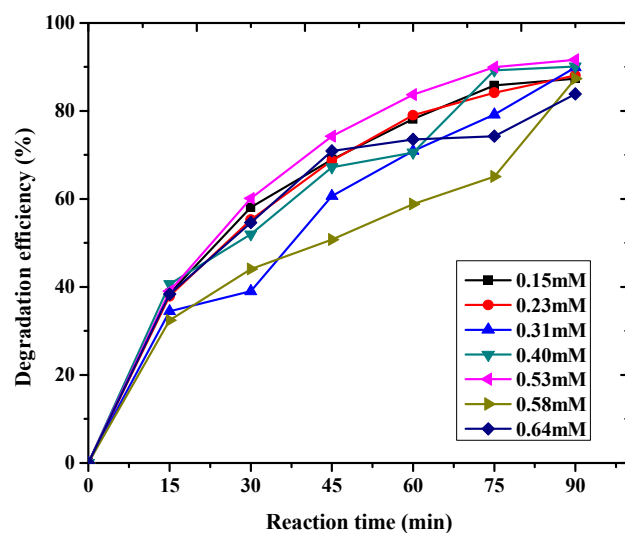


Fig. 6. The influence of phenol concentration on the degradation efficiency by $[C_{16}]_4H_2SiW_{10}V_2$ (0.80mM) with the hydrogen peroxide (0.23M) for 90 min

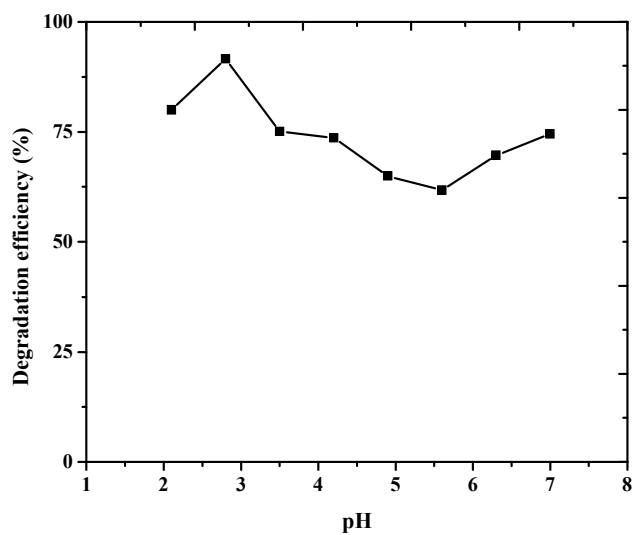


Fig. 7. The degradation efficiency of phenol (0.53mM) with H₂O₂ (0.23M) catalyzed by [C₁₆]₄H₂SiW₁₀V₂ (0.80mM) at different pH values for 90 min

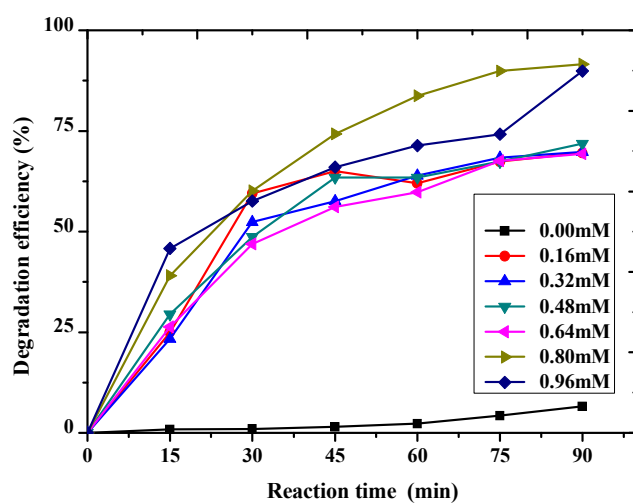


Fig. 8. The influence of the catalyst concentration on the degradation of phenol.

Reaction conditions: phenol solution (0.53mM), H₂O₂ (0.23M) for 90 min

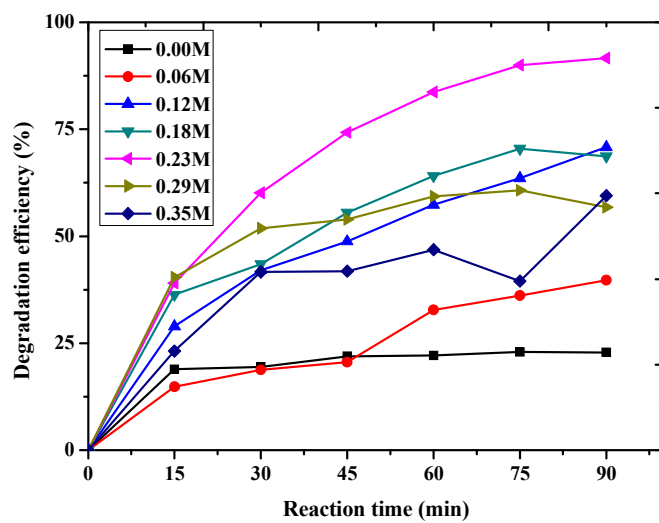


Fig. 9. The influence of H₂O₂ concentration on the degradation of phenol (0.53mM) by

[C₁₆]₄H₂SiW₁₀V₂ (0.80mM) for 90 min

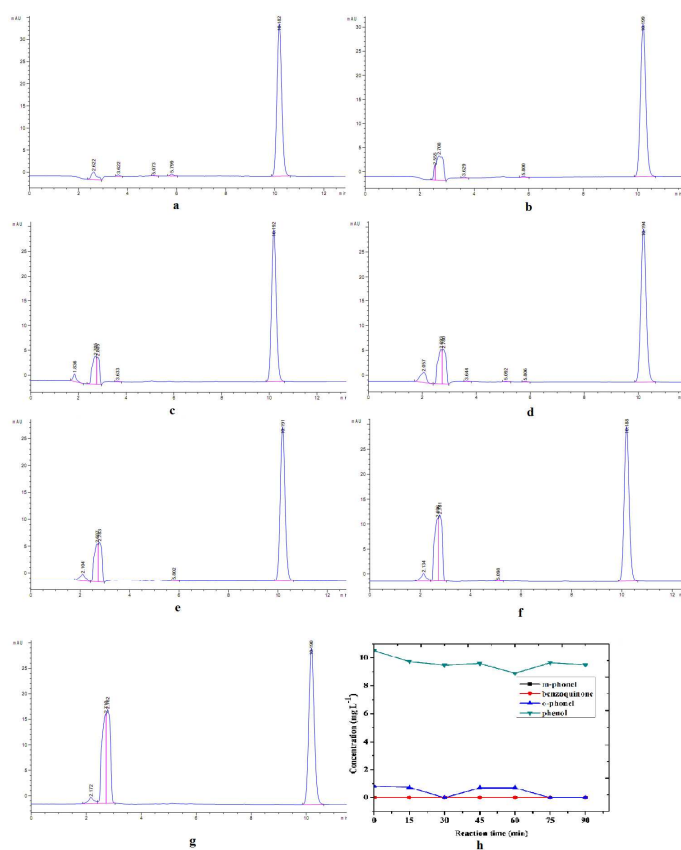


Fig. 10. The high performance liquid chromatography (HPLC) data of phenol (0.53mM) degradation intermediates at different time without $[C_{16}]_4H_2SiW_{10}V_2$ with the hydrogen peroxide (0.23M)

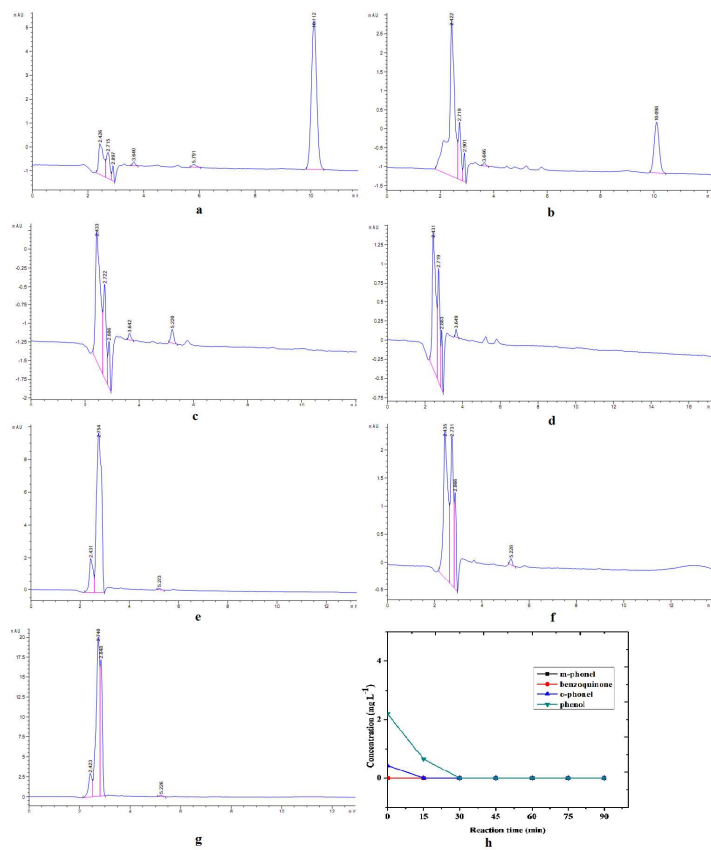


Fig. 11. The high performance liquid chromatography (HPLC) data of phenol (0.53mM) degradation intermediates at different time with $[C_{16}]_4H_2SiW_{10}V_2$ (0.80mM) with the hydrogen peroxide (0.23M)

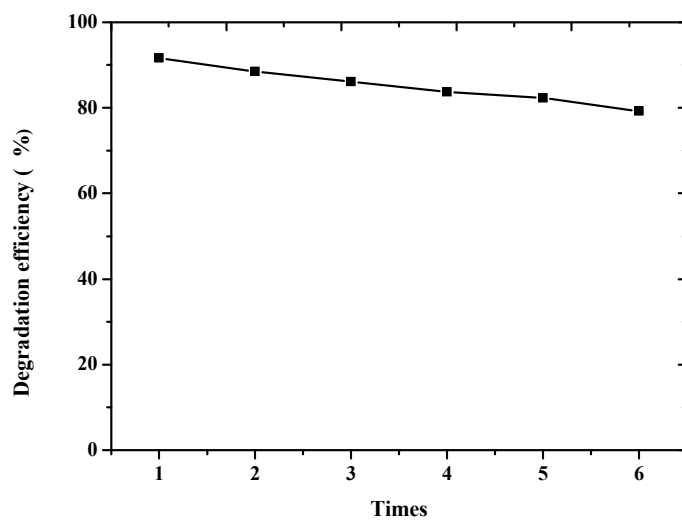


Fig. 12. Cycling runs in the degradation of phenol (0.53 mM) by $[C_{16}]_4H_2SiW_{10}V_2$ (0.80 mM) with H_2O_2 (0.23M) for 90 min