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Preparation and Antibacterial Property of Phosphomolybdic Heteropolyacid with Keggin Structures

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Abstract
Polyoxometalates have attracted great attention because of their high biological activity and low cost features. Three phosphomolybdic heteropolyacid with transition elements V as substituted atom were prepared by aether extraction in the acidic condition. They were charactered by XRD, FT-IR, UV-Vis, ICP and TG-DTA. Analysis results showed the molecular formula of $H_mPMo_{12-n}V_nO_{40}$ with Keggin structure. The antibacterial activities of $H_mPMo_{12-n}V_nO_{40}$ composites were tested for escherichia coli by the nephelometry method. The results indicated that the complexes showed obvious antibacterial effects on escherichia coli and the inhibition rate reached more than 70%. The activity can be improved more significantly with the increase of concentration of vanadium.

1. Introduction

Chemical material with antibacterial activity became more attractive in the development and application of fiber, transparent plastic film, paper and paint. Silver nanoparticles are being used as antimicrobial agents in many public places such as railway stations and elevators for many years, and they are said to show good antimicrobial action. However, it is a well-known fact that silver ions and silver-based compounds are highly toxic to microorganisms and have high cost features. [1, 2] Polyoxometalates (POMs), an intriguing class of metal–oxygen clusters, have attracted great attention because of their fascinating structural diversity, low cost and their potential applications in various fields, such as catalysis, gas storage, selective adsorption, magnetism, and medicine.[3,4] Till now, it has been found that there are more than 50 kinds of polyoxometalates with anti HIV property, almost involved in all series. Some other viruses have also different level of progress besides HIV, tumor, rheumatism. [5, 6] The biological activity of polyoxometalates is high selective inhibition of the enzyme function. However, it has seldom studies about their antibacterial activity as a function application. Molybdophosphoric acid and its vanadium-substituted products ($HPMoV_x$) were used as excellent materials in this field. [7, 8] Therefore, our research will be focus on the antibacterial activities of phosphomolybdic heteropolyacid on escherichia coli by the nephelometry method.

2. Experimental

2.1. Materials and Methods

All chemicals (AR) were purchased and used without further purification. Elemental analyses (C, N and H) were performed on Elemental Analyzer Perkin-Elmer Analyzer 2400 CHN. IR spectra were recorded in the range of 400-4000 cm^{-1} on a Perkin-Elmer 1730 FTIR spectrophotometer using KBr pellets. The phase structure of the plasma-treated powders was characterized by X-ray diffraction (JDX-3530M, Japan) using Ni-filtered Cu-$K\alpha$ radiation. UV-visible spectra were obtained using Shimadzu UV-2550 double beam instrument. Thermogravimetric analyses were performed on a Perkin-Elmer TGA-7, DTA-1700 Series. The TG-DTA experiments were carried out in N_2 from 20°C to 900°C, at the rate of $10°C\cdot min^{-1}$.

2.2. Synthesis of $H_mPMo_{12-n}V_nO_{40}$

Synthesis of the mono-, di- and trivanadium-substituted dodecamolybdophosphoric acids (samples V1, V2, and V3) was carried out according to the method of LOUIS[9] by acidifying with concentrated H_2SO_4 an appropriate mixture of solutions of Na_2HPO_4, Na_2MoO_4 and $NaVO_3$.

In the synthesis of $H_4PMo_{11}VO_{40}\cdot xH_2O$ (named V1), 3.58 g of $Na_2HPO_4\cdot 12H_2O$ and 26.65g $Na_2MoO_4\cdot 2H_2O$ were added to 50 mL of distilled, deionized water separately. The mixture was heated until reflux was achieved for 30 mins. Upon reaching reflux, a total of 1.22g $NaVO_3$ and H_2SO_4 acid (1:1) was added in three equal aliquots, approximately 10 min apart then pH reached to 2.0～2.5. After the 15 h had elapsed, the insoluble oxides had dissolved and a bright orange solution was formed. The liquid in the flask was evaporated and a bright orange solid was obtained. Orange block crystals were filtered off, washed with distilled water, and dried in a desiccator at 3°C-5°C temperature to give a yield of 37% with respect to Mo. $H_4PMo_{11}VO_{40}\cdot xH_2O$(marked as V1), $H_5PMo_{10}V_2O_{40}\cdot xH_2O$(V2)，$H_6PMo_9V_3O_{40}\cdot xH_2O$(V3).

The preparation procedure of V2 and V3 was similar to that of V1, ingredients ratio shown in Table 1.

Table 1. *Ingredients ratio of* $H_mPMo_{12-n}V_nO_{40}$.

	$Na_2HPO_4\cdot 12H_2O$/g	$Na_2MoO_4\cdot 2H_2O$/g	$NaVO_3$/g	pH
V1	3.58	26.6	1.22	2.0-2.5
V2	3.58	24.2	3.06	2.0-2.5
V3	3.58	21.8	4.29	2.0-2.5

3. Results and Discussion

3.1. Characterization of the Phase Structure

As shown in Fig.1, the XRD patterns of $H_mPMo_{12-n}V_nO_{40}$ were substantially similar to those reported, identifing as having a Keggin-type structure.[10] The strong absorption diffraction peaks are assigned to the range of 8°～10°, 16°～23° and 25°～30°. Similar experimental XRD patterns were found for compounds V1–V3, which shows that they are all isostructural.

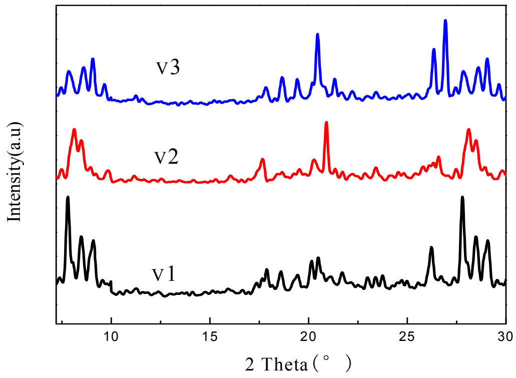

Fig. 1. *XRD patterns of* $H_mPMo_{12-n}V_nO_{40}$.

3.2. IR Spectra Analysis

The heteropolyacids prepared in this work revealed no well-defined powder X-ray diffraction pattern, thus eliminating the possibility of determining structural parameters in a straightforward manner. Instead, we used a variety of techniques including elemental analysis, thermal gravimetric analysis, and infrared spectroscopy to confirm that Keggin-type heteropolyacids were synthesized.

Fortunately, the Keggin-type heteropolyacid has four well-defined infrared bands in the range 700–1100 cm^{-1} that can be used for positive identification [10]. Fig. 2 presents the infrared spectra of our samples $H_mPMo_{12-n}V_nO_{40}$ dissolved in acetone with the appropriate bands labeled by arrows. The sample exhibited the characteristic stretches associated with the Keggin structure. Evidently, the synthetic method used here produced Keggin-type heteropolyacids, the strong bands at 959 cm^{-1} arise from stretching vebration of terminal Mo–O. The bonds at 792 cm^{-1} and 868cm^{-1} are attributed to ν_{as} Mo–O–Mo stretching. The 1058 cm^{-1} bands stem from ν P-O. The 1622 cm^{-1} band is due to ν_{as}O–H stretching.

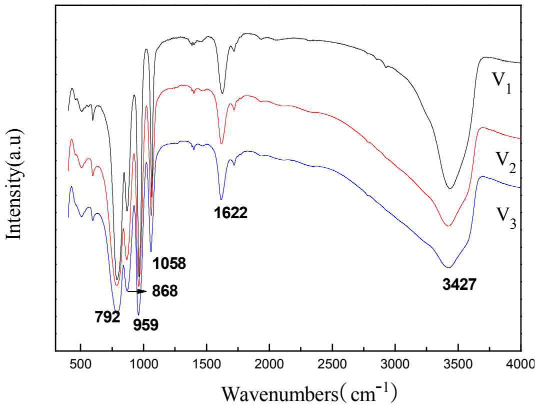

Fig. 2. *IR spectrum of* $H_mPMo_{12-n}V_nO_{40}$.

3.3. UV Spectra Analysis

Ultraviolet–Visible reflectance spectroscopy provided additional information about the substitution of ions into the Keggin units of the heteropolyacids. As shown in Fig. 3, the samples exhibited the typical sharp absorption threshold in the UV region. Compounds 1–3 exhibit photoluminescent properties at room temperature. The maximum emission peak of compound V1 is located at 250nm and 310 nm, which due to the charge transfer of end oxygen to Mo and bridge oxygen to Mo respectively. [10] Compounds V2 and V3 exhibit photoluminescent properties similar to those of compound V1. Therefore, results from both UV–Vis and IR spectroscopies suggest the samples prepared with Keggin units.

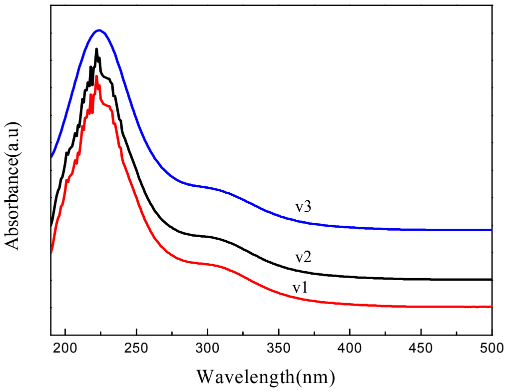

Fig. 3. *UV-Vis spectra of* $H_mPMo_{12-n}V_nO_{40}$.

3.4. Composition Analysis (ICP)

In Table 2, the results from elemental analysis of our synthetic samples are compared to the theory value of phosphomolybdic acid. The Mo/P ratio of the standard (ideal formula $H_3PMo_{12}O_{40}$) was 12, indicating a relatively pure phase of the heteropolyacid. The Mo/P ratios in our synthesized PMoV samples were 11.1, 9.6 and 8.4, respectively, which are consistent with slightly lower contents of Mo in the Keggin units due to partial substitution of Mo by V cations. Indeed, the V/P ratio in both samples was around 0.8.

Table 2. *Elemental analyses of* $H_mPMo_{12-n}V_nO_{40}$ *(Calculated result).*

	V1	V2	V3
P(%)	1.50(1.54)	1.53(1.57)	1.48(1.52)
Mo(%)	51.21(52.38)	47.33(48.68)	42.04(42.44)
V(%)	2.48(2.53)	4.98(5.17)	7.48(7.51)

3.5. Thermogravimetry Analysis

Fig. 4 presents the TG results for each sample and illustrates the mass loss associated with evolution of this so-called protonic water. The temperature for TG experiment ranged from 50°C to 350°C. They show similar weight-loss stages. In the TG curve of V1, the first weight loss between 50 and 80°C corresponds to a loss of crystallographic water. The second weight loss step in the range 80–170°C corresponds to the release of coordinated water molecules. Therefore, during 270°C, the compound V3 cluster decomposes. The number of crystallization water was calculated according to the weight proportion: 9.7131, 11.2176 and 3.6505. Results from both elemental and thermal gravimetric analyses provide some evidence for the presence of Keggin units in the samples: $H_4PMo_{11}VO_{40}•10H_2O$, $H_5PMo_{10}V_2O_{40}•11H_2O$ and $H_6PMo_9V_3O_{40}•4H_2O$.

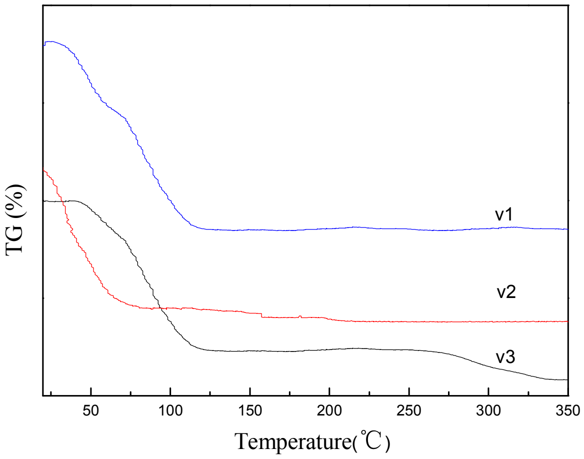

Fig. 4. *TG analysis of* $H_mPMo_{12-n}V_nO_{40}$.

3.6. Antibacterial Property

The strains were obtained from 7.5% NaCl broth under sterile conditions, and then were cultured in 37°C for 24 h. The Nephelometry method was used for antibacterial experiments with no compounds as blank sample.[11] The twice activation of the experimental species were prepared by the NB culture with the concentration of 10^6 CFU·mL^{-1}. The compounds were dissolved in test tubes with the concentration of 256μg·mL^{-1}, the of the title compound with was adjusted to zero, The OD_{600} was determined with no bacteria solution as blank in 37°C for 20 h. The inhibition rate (I) was calculated by the formula as follows:

$$i = \frac{OD_0 - OD}{OD_0} \times 100\%$$

The absorbance of OD was the blank, and the absorbance value was measured by ultraviolet visible spectrophotometer. The antibacterial property of the compounds was shown in Table 3.

Table 3. *Antibacterial property of Mo-P-V Serials.*

	Blank (Abs)	Sample (Abs)	Inhibition rate (*i*/%)
V3	2.560	0.124	90.62
V2	2.560	0.298	88.36
V1	2.560	0.732	71.41

The hetropolyacids of the series $H_mPMo_{12-n}V_nO_{40}$ showed good to excellent antibacterial behaviors. The results are shown in Table 3. V3 antibacterial efficiently gives a total yield of 91% with Nephelometry method. The yield with this property was found to decrease from 91% to 71%. In other words, the antibacterial activities of the $H_mPMo_{12-n}V_nO_{40}$ were found to decrease in the following order: $H_6[PMo_9V_3O_{40}]$>$H_5[PMo_{10}V_2O_{40}]$ >$H_4[PMo_{11}VO_{40}]$.

Many properties of the heteropoly compounds in solution depend on the reaction time, the solvent type, the structure of the catalyst, the pH value of the solution, and other factors. The Keggin anion has an assembly of 12 corner-shared octahedral MoO_6 from trimetallic groups $[Mo_3O_{13}]$ around a heteroatom tetrahedron PO_4 [12]. The introduction of vanadium (V) into the Keggin framework of $[PMo_{12}O_{40}]^{3-}$ is beneficial for antibacterial processes. Usually positional isomers coexist when two or more vanadium atoms are incorporated into the Keggin structure. [13] Studies on these isomers in antibacterial processes indicated that different isomers displayed different reactivities. [14-16] The efficiency is related to the mol percentage of metal atoms. As the V species present in all of the compounds were set to the same content (V, 0.039 mmol), the amount of V present in the system, is suggested to govern the antibacterial activity. The activity can be improved more significantly with the increase of percentage of vanadium.

Our findings have shown that the antibacterial activities can be improved more significantly with the increase of concentration of vanadium occurred in the order of: HPMoV3>HPMoV2>HPMoV1. It is suggested that, besides energy and composition of the LUMO, the presence of both Bronsted acidity and vanadium in the structure of mentioned heteropolyacids are responsible for antibacterial activity. The greater protons number may lower the activation energy barrier, and the greater vanadium atoms may provide many sites for antibacterial process. Also, by increasing the value of x in the HPMoVx formula, the antibacterial activities can be improved regularly.

4. Conclusion

The $H_mPMo_{12-n}V_nO_{40}$(n=1, 2, 3) compounds were prepared by aether extraction in the acidic condition. The combined results of elemental analysis, thermal gravimetric analysis, elemental analysis, IR, UV–Vis, and XRD provide a reasonable description of the polyoxometalates prepared by the methods described above. The PMoV sample is a Keggin-type phosphomolybdic acid, and has V substituting for Mo in the Keggin structure. The antibacterial activities of $H_mPMo_{12-n}V_nO_{40}$ composite were tested for escherichia coli by the nephelometry method and improved with the increase of concentration of vanadium. Therefore, it provides new serials compounds for the development of low toxicity and high efficiency antibacterial activity materials.

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