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Synthesis and Characterization of Tungstophosphoric Heteropolyacid ($H_5PW_{11}TiO_{40}$) Containing Titanium

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The tungstophosphoric heteropolyacid ($H_5PW_{11}TiO_{40}$) contained titanium was prepared and then characterized by FT-IR, UV, XRD and TG/DSC analysis, which revealed that the $H_5PW_{11}TiO_{40}$ heteropolyacid was Keggin structure and one $H_5PW_{11}TiO_{40}$ heteropolyacid molecule contained fifteen crystal water molecules ($H_5PW_{11}TiO_{40}·15H_2O$). And the tungstophosphoric heteropolyacid ($H_5PW_{11}TiO_{40}$) contained titanium could be used as a green catalyst for cleaner reactions.

Keywords: Tungstophosphoric, Heteropolyacid, Keggin, Titanium.

INTRODUCTION

Heteropolyacids have been found broad applications in both industrial and preparative chemistries due to their unique physical and catalytic properties, ability to work in different multiphase systems and easiness and low cost of their preparation[1]. A number of the heteropolyacids catalyzed processes has been commercialized and many interesting and promising examples of their catalytic application for various types of transformations in both homo- and heterogeneous systems are currently under study[2-6].

Heteropolyacids are transition metal oxygen anion clusters that exhibit a wide range of molecular sizes, compositions and architectures[7] and the economically feasible solid catalysts can offer several advantages, such as excellent solubility in water, high catalytic activities and reactivates, ease of handling, cleaner reactions in comparison to conventional catalysts (less waste production), non-toxicity and experimental simplicity. Thus, heteropolyacids have long been known to be good catalysts for in different reactions, such as dehydration[8], esterification[9], acetalization synthesis[10].

In this work, the tungstophosphoric heteropolyacid ($H_5PW_{11}TiO_{40}$) contained titanium was prepared and characterized by FTIR, UV, XRD and TG/DSC methods. Furthermore, we proved further that the $H_4PW_{11}TiO_{40}$ heteropolyacid was typical Keggin structure.

EXPERIMENTAL

All chemicals were analytical grade and were used without further purification. $Na_2HPO_4·12H_2O$, $Na_2WO_4·2H_2O$ and $Ti(SO_4)_2$ were purchased from Sigma Chemical Co. Ltd. (Shanghai, China). And ether, H_2SO_4, H_2O_2 were all purchased from Chongqing Medicines. Co. Ltd (Chongqing, China).

Synthesis of the tungstophosphoric heteropolyacid ($H_5PW_{11}TiO_{40}$): The heteropolyacid was prepared by a method[7]. The details of the procedure for the preparation of $H_5PW_{11}TiO_{40}$ heteropolyacid were the following: 8.9 g of $Na_2HPO_4.12H_2O$ was dissolved in 250 mL distilled water and 6 g of $Ti(SO_4)_2$ was dissolved in 100 mL of 2 mol L^{-1} H_2SO_4 solution. They were mixed and heated until boiling. After 0.5 h, 400 mL solution containing 90.7 g of $Na_2WO_4·2H_2O$ was added into the above solution at 90 °C for 0.5 h. Then, 1:1 H_2SO_4 was added (dropwise and with stirring) to the solution until pH 2. The mixture was cooled to room temperature under stirring and 50 mL ether was added. The middle oil-like red material was heteropolyacid-ether compound until three layers appeared in the solution after thorough shaking and was then separated. The heteropolyacid was washed with a suitable amount of distilled water and dried under vacuum for about 2 days. The resulting fine orange powders were characterized by all kinds of methods.

Characterization of the tungstophosphoric heteropoly-acid ($H_5PW_{11}TiO_{40}$) The Fourier transform IR (FT-IR) spectrum was recorded on a Perkin-Elmer GX spectrometer (Perkin-Elmer, USA) on KBr discus. The ultraviolet-visible absorption spectrum was conducted on a UV-2550 spectrometer. The XRD spectrum was tested on a XRD 6000 diffractometer (Shimadzu, Japan) with CuKα ray (λ = 0.15418 nm) under 5-40 °/2θ scanning style and TG/DSC analysis were carried out with STA449C instrument (Netzsch, Germany) under an argon atmosphere at a heating rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION

Fig. 1 shows the FT-IR spectrum of the the tungstophosphoric heteropolyacid ($H_5PW_{11}TiO_40$) and the pure $H_5PW_{11}TiO_{40}$ exhibit typically four major IR bands located at 1080, 983, 890 and 804 cm^{-1} attributed to absorption modes of Keggin ion $[PW_{11}TiO_{40}]^{5-}$. And the four bands at 1080, 983, 890 and 804 cm^{-1} are assigned to the stretching modesof oxygen atom bond to tungsten and phosphorous, P-O, W=O, W-O-W in corner shared octahedral and W-O-W in edge shared octahedral, respectively[11]. Two peaks at 3402 and 1618 cm^{-1} represented stretching vibration and deformation vibration of O-H in crystal water, respectively. In the heteropolyacid, it is observed the characteristic bands of Keggin structure and similar results were also observed by Kulkarni *et al.*[11] and Ferreira *et al.*[12].

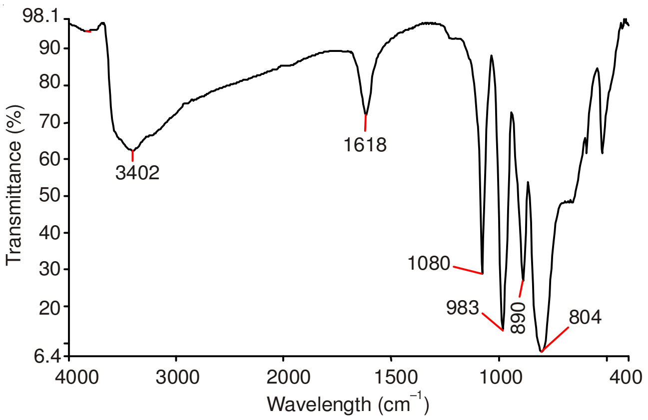

Fig. 1. FITR spectrum $H_5PW_{11}TiO_{40}$ heteropolyacid

There are charge transfer transition spectrum and coordinate field spectrum in the electronic spectrum of heteropolyacid compound, therefore, two visible absorption peaks could be seen in the ultraviolet spectrum. In the heteropolyacid compound for its Keggin structure, the absorption peak of M=O (M: metal atom) band is usual appearance in high field for its double bond, therefore, the absorption band of M-O-M can be seen in low field. In the Fig. 2, there show two evident absorption peaks at about 210 and 260 nm, and they were ascribed to charge transfer transitions of W=O and W-O-W for anion $[PW_{11}TiO_{40}]^{5-}$ in the heteropolyacid, respectively, which revealed that the $H_5PW_{11}TiO_{40}$ heteropolyacid prepared in our laboratory has typical Keggin structure.

The XRD patterns of the heteropolyacid are shown in the Fig. 3. For 1:11 [P: M] (P: phosphorus ; M: metal atom) serial heteropolyacid with Keggin structure, the characteristic diffraction peaks could be seen at 7-12°, 16-22° and 25-32°.

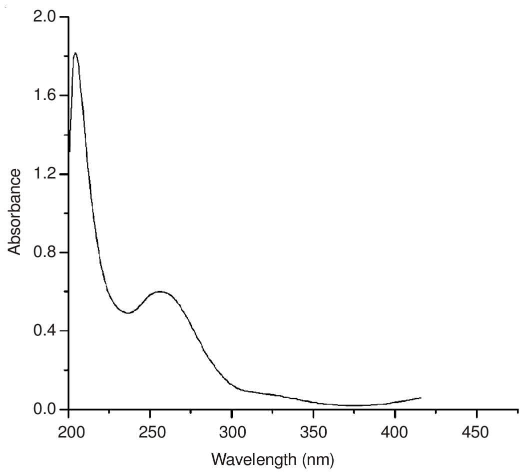

Fig. 2. UV spectrum $H_5PW_{11}TiO_{40}$ heteropolyacid

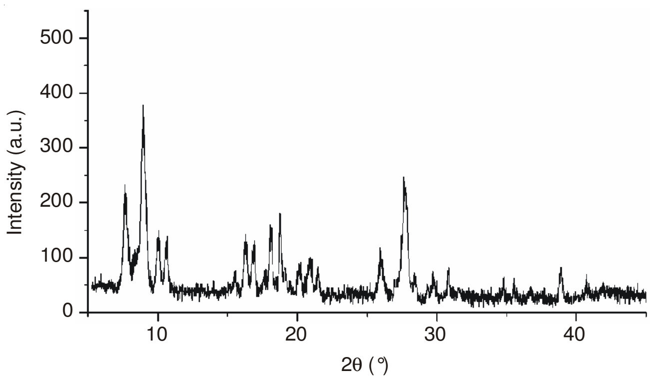

Fig. 3. XRD pattern diagram $H_5PW_{11}TiO_{40}$ heteropolyacid

In the Fig. 3, these diffraction peaks show in the three spans mentioned and could be observed similar behavior with Keggin structure heteropolyacid and these results revealed that we had prepared the $H_5PW_{11}TiO_{40}$ heteropolyacid with Keggin structure successfully.

The stability of the $H_5PW_{11}TiO_{40}$ heteropolyacid was assessed by TG/DSC analysis (Fig. 4), which showed two evident endothermic peaks in the TG/DSC diagram (Fig. 4) at 83.3 and 202.2 °C, respectively. The Fig. 4 showed that heteropolyacid was stable up to 250 °C and the about weight loss of 9 % below 250 °C was corresponded to the release of hydrated water. The results revealed that one $H_5PW_{11}TiO_{40}$ heteropolyacid molecule contained fifteen water molecules and the complex's formula should be $H_5PW_{11}TiO_{40}\cdot 15H_2O$. However, the exothermic peak at 202.2 °C indicated that there was stronger combined strength between proton and water molecular for the better acidity of the heteropolyacid with tungsten atom[13].

Conclusion

The tungstophosphoric heteropolyacid ($H_5PW_{11}TiO_{40}$) has been synthesized and then well characterized by FT-IR, UV, XRD and TG/DSC and which revealed that we had prepared the $H_5PW_{11}TiO_{40}$ heteropolyacid with Keggin structure successfully. According to the TG/DSC analysis, these results indicated that one $H_5PW_{11}TiO_{40}$ heteropolyacid molecule contained fifteen crystal water molecules and the complex's formula should be $H_5PW_{11}TiO_{40}\cdot 15H_2O$ and it could be used to cleaner reactions as a green catalyst.

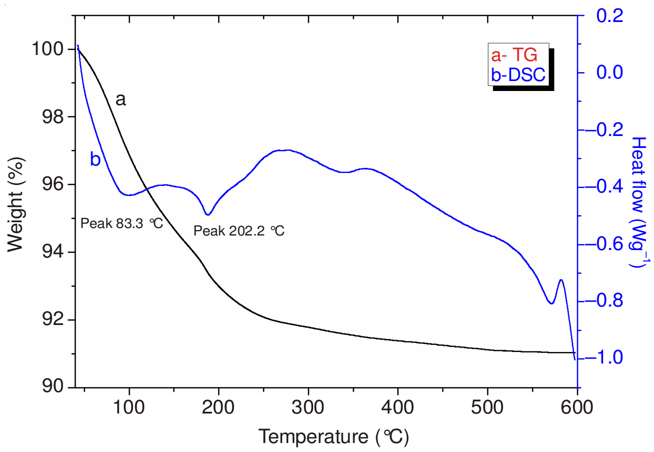

Fig. 4. TG/DSC diagram $H_5PW_{11}TiO_{40}$ heteropolyacid

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