Synthesis and Characterization of Heteropoly Complex of Magnesium-substituted Zinc-centred Undecatungstate Ligand

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Abstract. New Magnesium-substituted heteropoly undecatungstozincate complex with Keggin structure, K_8 [Mg (H_2O) $ZnW_{11}O_{39}$] $\cdot 13H_2O$, was synthesized by the stepwise acidification and the stepwise addition of materials. The product was characterized by ICP, IR spectrum, UV spectrum, X-ray power diffraction and thermal analysis.

1. Introduction

Heteropoly acids and heteropoly complexes, negatively charged early transition metal oxide clusters, are formed by inorganic metal–oxygen cluster anions with special structures, and they can be applied in many areas, such as catalysts for organic reactions, dopants in sol-gel matrixes, corrosion resistant coatings, membranes in selective electrodes, gas detection apparatus, liquid and solid electrolytic cells, solid-state electrochromic devices, sensors and hydrogen-oxygen fuel cells [1-7]. The synthesis of mixed heteropoly complexes is a frontal work in the basic studies on heteropoly compounds. 11 tungsten unsaturated heteropoly anion as a ligand can form mixed heteropoly anion with transition elements, rare earth elements and main group element ion. The heteropoly anion structure is 1:12 the Keggin structure of lost as a W-O_d. Due to the heteropoly complexes have the catalytic activities and antiviral properties with the reactions of some organic synthesis [8-15]. The synthesis of novel complex is still attracting people's attention. The synthesis and characterization of the new heteropoly complex K_8 [Mg (H_2O) $ZnW_{11}O_{39}$] $\cdot 13H_2O$ are described in the paper.

2. Experimental

2.1. Synthesis

K_8 [Mg (H_2O) $ZnW_{11}O_{39}$] $\cdot 13H_2O$ was synthesized according to recent literature source [16]. 0.11 mol sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) was dissolved in 200 mL distilled water. The solution was adjusted to pH~6.3 with acetic acid and was heated to boil. After that, 40 mL hot weak acidic aqueous solution which contained 0.01 mol zinc sulfate solution ($ZnSO_4 \cdot 7H_2O$) was added dropwise to the above solution with stirring. The mixture was continuously heated at 100 ℃ for 30 min, a solution of 30 mL 0.01 mol of magnesium sulfate ($MgSO_4$) was dropwise added to the mixture with stirring. The pH was readjusted to 5.0 and stirring was continued for 1.5 h. Finally, the cooled

solution was extracted with 30mL absolute alcohol. A white oily matter was obtained. Dissolving it with boiled distilled water, and then adding 25g KCl and stirring for several minutes at room temperature. The oily product was precipitated, and then extracted by dissolving-cooling method for several times.

2.2. Instruments and reagents

Infrared spectrum (IR) was recorded on a Perkin- Elmer 1730 FT/IR spectrometer with KBr pellets. The UV spectrum was measured on a PERSEE TU-1901 spectrophotometer in water solution. X-Ray powder diffraction analysis was obtained on a BRUKER D8 ADVANCE X-ray diffractometer. The thermal stability of the sample was investigated using simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) techniques. The measurement was performed using a NETZSCH STA 449C thermal analyzer in a nitrogen stream, with a scanning rate of $10\,°C\,min^{-1}$. An 8410 ICP spectrometer was also used.

2.3. Elemental Analysis

Potassium, magnesium, zinc, and tungsten were by ICP spectrometry. The water content was determined by thermogravimetry. Elemental anal.(%) calcd. for $K_8[Mg(H_2O)ZnW_{11}O_{39}]\cdot 13H_2O$: K 9.86, Mg 0.73, Zn 1.98, W 61.28, H_2O 7.6; Found: K 9.77, Mg 0.72, Zn 1.95, W 60.88, H_2O 7.55.

3. Results and discussion

3.1. IR Spectra

Infrared spectroscopy is an effective method for studying the structure [17]. The best feature area of the spectrum is around $1100–700\ cm^{-1}$ are observed, due to the absorption of metal-oxygen stretching vibrations [18-19]. In the IR spectrum of $K_8[Mg(H_2O)ZnW_{11}O_{39}]\cdot 13H_2O$ as shown Figure 1, there are four bonds: $\nu_{as}(W\text{-}O_d)$, $933\ cm^{-1}$; $\nu_{as}(W\text{-}O_b\text{-}W)$, $862\ cm^{-1}$; $\nu_{as}(W\text{-}O_c\text{-}W)$, 797 and $748\ cm^{-1}$; $\nu_a (Zn\text{-}O_a)$, 443 ans $418\ cm^{-1}$. These characteristic vibration patterns of $K_8 [Mg (H_2O) ZnW_{11}O_{39}]\cdot 13H_2O$ indicate the heteropoly complex still maintains Keggin structure.

The vibrational frequencies fall in the sequence of $\nu_{as} (W\text{-}O_d) > \nu_{as} (W\text{-}O_b\text{-}W) > \nu_{as} (W\text{-}O_c\text{-}W)$, which are assigned to $W\text{-}O_d$ stretching, stretching of $W\text{-}O_b\text{-}W$ inter bridges between corner-sharing WO_6 octahedra and bending of $W\text{-}O_c\text{-}W$ inter bridges between edge-sharing WO_6 octahedra at $700~1100\ cm^{-1}$. These bands can be easily identified and confirm the formation of this hybrid molecular complexes Additionally, two evident peaks in the range of 3351 and $1623\ cm^{-1}$ correspond to the stretching vibration of O-H bonds and the bending vibration of H-O-H bonds, respectively.
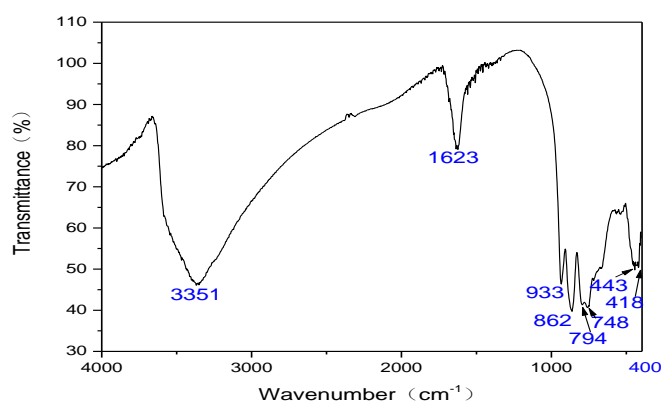
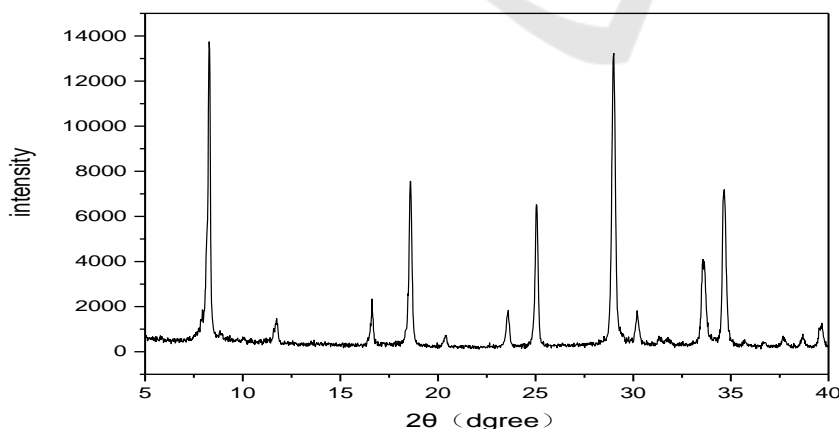**Figure 1.** IR spectrum of $K_8 [Mg (H_2O) ZnW_{11}O_{39}]\cdot 13H_2O$.

3.2. UV Spectra

The heteropoly complexes are generally characterized by oxygen-to-metal (O-M) charge transfer bands, which appear in the UV region below 400 nm. The UV spectrum data for the complex is given in Figure 2. There is an intense absorption peak at 192 nm, which can be considered as the terminal oxygen ($O_d \rightarrow W$). Similarly, a relatively weak absorption peak at 261 nm can be regarded as the charge-transfer of the bridge oxygen to metal atoms ($O_b/O_c \rightarrow W$). So there is evidence of the characteristic bands of Keggin structure of the heteropolytungstates [20].
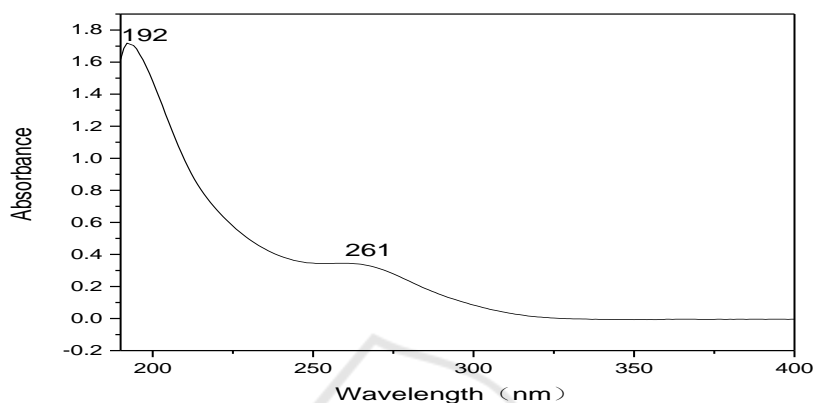
Figure 2. UV spectrum of $K_8 [Mg(H_2O)ZnW_{11}O_{39}] \cdot 13H_2O$.

3.3. X-ray powder diffraction

X-ray diffraction analysis is used extensively to study the structure of heteropoly complexes [21-22]. The result of X-ray powder diffraction (XRD) of the product is shown in Figure 3. The most intense peak exists at about 8.28° for $K_8 [Mg (H_2O) ZnW_{11}O_{39}] \cdot 13H_2O$. The Bragg reflection peaks which exist in four ranges of 2θ (i.e. 7~10°, 16~22°, 25~30° and 33~38°) are the characteristic peaks of the heteropoly complex with Keggin structure, showing that the target product has high crystallinity.
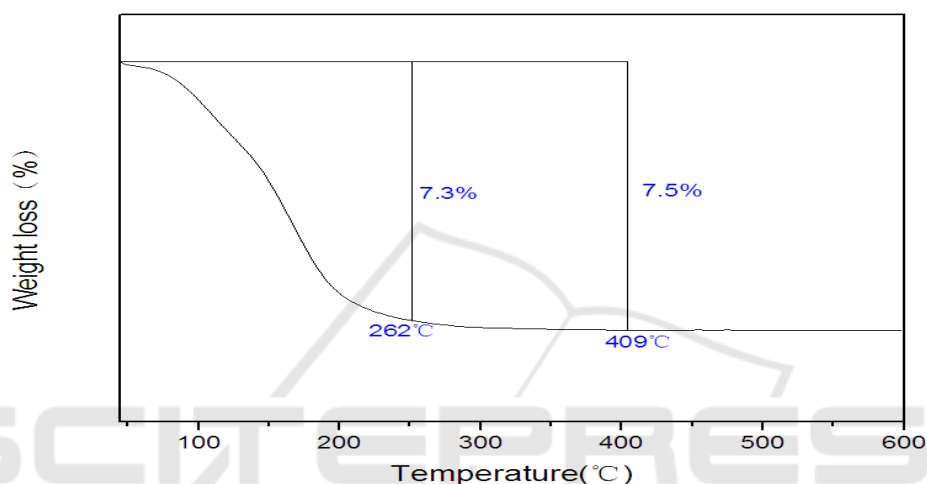

Figure 3. XRD pattern of $K_8 [Mg (H_2O) ZnW_{11}O_{39}] \cdot 13H_2O$.

3.4. Thermal analysis

Figure 4 shows the TG curve of the heteropoly complex. Heteropoly complex is usually obtained with a large amount of water of crystallization [23]. Three types of water molecule can be distinguished in these solids: hydration water, zeolite water and structural water. The TG curve shows a major weight loss of 7.5% for the heteropoly complex below 409 ℃, which demonstrates that 14 water molecules have been lost for the heteropoly complex. There are almost 13 molecules of hydration water below 262 ℃ for the heteropoly complex and finally the loss of 1 molecule of structural water at 409 ℃ for the heteropoly complex. So the accurate molecular formula of the heteropoly complex can be assigned as $K_8[Mg(H_2O)ZnW_{11}O_{39}]\cdot 13H_2O$.

In general, we take the temperature of the exothermic peak of DTA curve as the sign of their thermostability. In the curve, there is an exothermic peak at 470 ℃, at which the product decomposes.

Figure 4. TG curve of $K_8[Mg(H_2O)ZnW_{11}O_{39}]\cdot 13H_2O$.

4. Conclusions

The synthesis and characterization of the heteropoly complex of magnesium with undecatungstozincate is reported in this paper. The composition and structure of the complex was determined by means of ICP and XRD. TG curve show that the weight loss of the product is a two-step process. The results show that the general formula is $K_8[Mg(H_2O)ZnW_{11}O_{39}]\cdot 13H_2O$ and the structure of the product derives from the Keggin structure. The IR and UV spectra of the complex were investigated. And the synthesized product possess potential application prospect for catalysis.

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