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Thermal stability of ternary transition metal heteropoly complexes

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Abstract

The thermal stability in air of ternary transition metal heteropoly complexes with 11-tungstic transition metal heteropolyanions as ligands has been investigated by TG-DTA, XPS, IR at different temperatures and solubility tests. The results indicate that the thermal stability of the complexes is correlated with that of the lacunar heteropolyanion ligands.

Keywords: 11-Tungstic transition metal; Heteropoly complex; Thermal stability

1. Introduction

Studies on substituted heteropoly complexes are at the forefront of basic studies on heteropoly compounds because the substituted heteropoly complexes have unique properties, such as acidity, oxidation–reduction and thermal stability. The substituted heteropoly complexes with Keggin structure have various promising applications as catalysts and proton conductors [1,2].

The 11-tungstic series of lacunar hereopoly anions ($MW_{11}O_{39}$) retain the Keggin structure, with loss of a W–O group. The lacunar hereopoly anions ($MW_{11}O_{39}$) that are highly reactive can form ternary heteropoly complexes with metal cations. The ternary heteropoly complex $K_m[Z(H_2O)MW_{11}O_{39}]\cdot xH_2O$ is formed when a transition metal cation of the fourth period or a group IIIA cation enters into the vacancy. For $K_m[Z(H_2O)MW_{11}O_{39}]\cdot xH_2O$, which retains the Keggin structure [3], 11-tungstic heteropolyanion acts as a five-dentate ligand and the sixth location is occupied with structural water. Similarly, $K_n[Ln(MW_{11}O_{39})_2]\cdot yH_2O$ is formed when a lanthanide enters into the vacancy. For $K_n[Ln(MW_{11}O_{39})_2]\cdot yH_2O$, there are two 11-tungstic heteropolyanions that act as four-dentate ligands and every four oxygen atoms around the vacancy of the ligand combine with a Ln atom to form square antiprism complexes [4].

We synthesized the heteropoly complexes $K_m[Z(H_2O)MW_{11}O_{39}]\cdot xH_2O$ (expressed as ZMW_{11}) and $K_n[Ln(MW_{11}O_{39})_2]\cdot yH_2O$ (expressed as $Ln(MW_{11})_2$) (M = Cr, Mn, Fe, Co and Cu). In this paper, the thermal stability of the ternary transition metal heteropoly complexes is reported.

2. Experimental

2.1. Instrument and reagents

Thermal analysis (TG and DTA) was carried out on a Q-Derivatograph thermal analyzer with a rate of temperature increase of 10 °C/min, using α-Al_2O_3 as the standard substance. IR spectra were obtained with an Alpha Centauri FT infrared spectrometer. XPS was measured on a ESCALAB-MARK-II diffractometer with C_1s level as the standard, using Mg Kα X-ray as the excitation source.

2.2. Preparation

ZMW_{11} and $Ln(MW_{11})_2$ were prepared according to the literature [5].

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3. Results and discussion

Generally, we take the temperature of the exothermic peak of DTA curves as a criterion for thermal stability of heteropoly complexes [6]. The temperature of the exothermic peak is higher than the decomposition temperature, but is correlated with the decomposition temperature. The exothermic peak is attributed to the crystallization of the decomposition product. The temperatures of the exothermic peak of DTA curves are assembled in Table 1.

The thermograms of $Sm(CuW_{11})_2$ and $NiCrW_{11}$ are shown in Figs. 1 and 2, respectively.

The TG curve of $NiCrW_{11}$ (Fig. 2) shows that the weight loss of ZMW_{11} occurs in two steps. The first step of $NiCrW_{11}$ weight loss that occurs below 175 °C is a continuous process. Correspondingly, there is a big endothermic peak at 86 °C in the DTA curve. And $NiCrW_{11}$ is soluble in water at 86 °C, which is suggested by the solubility test. Therefore, it is reasonable for us to assume that the first step is the loss of the zeolite water while the second step that occurs between 175 and 400 °C is the loss of ligand water.

Table 1
Temperature of exothermic peak in DTA curve

T (°C)	Fe^{3+}	Co^{2+}	Ni^{2+}	Zn^{2+}	Al^{3+}	Ga^{3+}
CrW_{11}	441	393	400		420	
MnW_{11}			376	382		390
FeW_{11}					470	
CoW_{11}					436	
CuW_{11}	425	385	390	386	400	418

T (°C)	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy
CrW_{11}	425			430	423			
MnW_{11}	405			404		404	405	406
FeW_{11}				482	485	482	486	490
CoW_{11}			451		452	452	451	
CuW_{11}	407	407	409	406	412	408	406	406

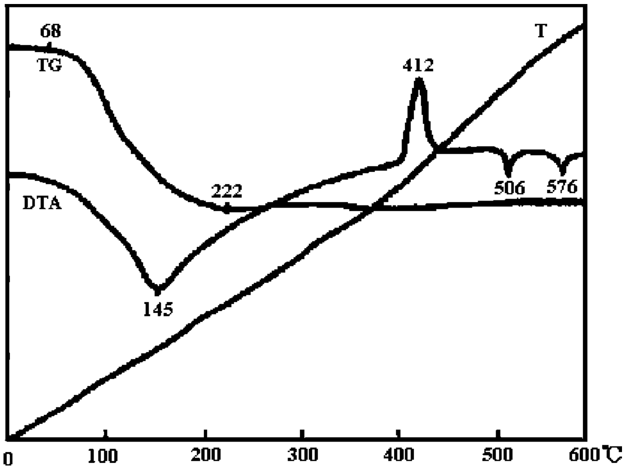

Fig. 1. TG and DTA curves for $Sm(CuW_{11})_2$.

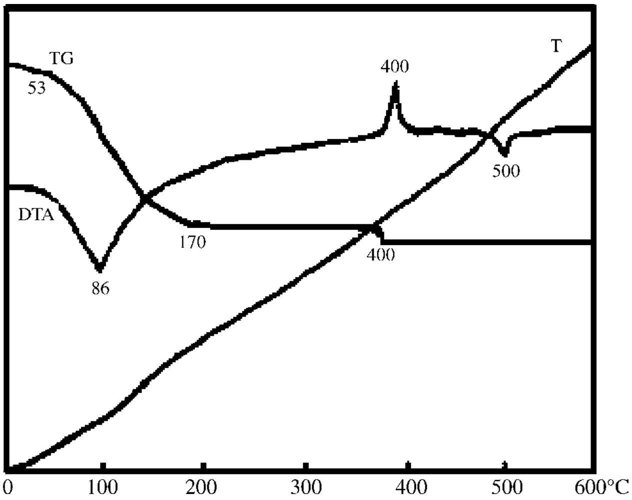

Fig. 2. TG and DTA curves for $NiCrW_{11}$.

The weight loss of $Ln(MW_{11})_2$ occurs only in one step. The TG curve of $Sm(CuW_{11})_2$ (Fig. 1) shows that the weight loss occurs in a continuous step below 222 °C and correspondingly there is a big endothermic peak at 145 °C in the DTA curve. The IR spectrum (Fig. 3), which has no obvious change, shows that the ν_{as} (W–O_d) and ν_{as} (W–O_b–W) still exist at 145 °C. And the solubility test shows that $Sm(CuW_{11})_2$ is soluble in water at this temperature. Therefore, it is impossible for the complex to decompose at 145 °C. Clearly, it is the zeolite water or the water weakly bonded to balancing-ions and the water between $Ln(CuW_{11})_2$ molecules that is lost below 222 °C. All the water molecules in the $Sm(CuW_{11})_2$ coordinate around the potassium cation or between the $Sm(CuW_{11})_2$ molecules. There are no zeolite water molecules in the $Sm(CuW_{11})_2$ molecules.

The endothermic peaks in the DTA curve at high temperature have no corresponding changes in the TG curve, indicating that it is the fusion of the decomposition product.

Both the formation of the W–O–W bridge bond and the existence of W=O_d, which has partial properties of a double bond, are an important sign of the formation of heteropoly complexes and their derivatives. The W–O–W bridge bond and W=O_d are different in the thermal stability: W=O_d is more stable and the intensity of its vibration absorption decreases at a slow rate when the temperature increases. Therefore, the changes of the bond stability can be determined by solubility tests in water and the IR spectra of the sample which has been heated at different temperatures for half an hour.

Fig. 3 shows that below 380 °C, the vibration frequencies of W–O–W and W=O_d change little compared with those under normal condition. But after being heated at 380 °C, still a part of the product can dissolve in water, which indicates that below 380 °C, though the W–O–W bond and W=O_d are not completely broken, the $Sm(CuW_{11})_2$ has begun to decompose. What is more, when putting some of the product that has been treated at 350 °C into water, there is already a small quantity of substance that is insoluble in water. The

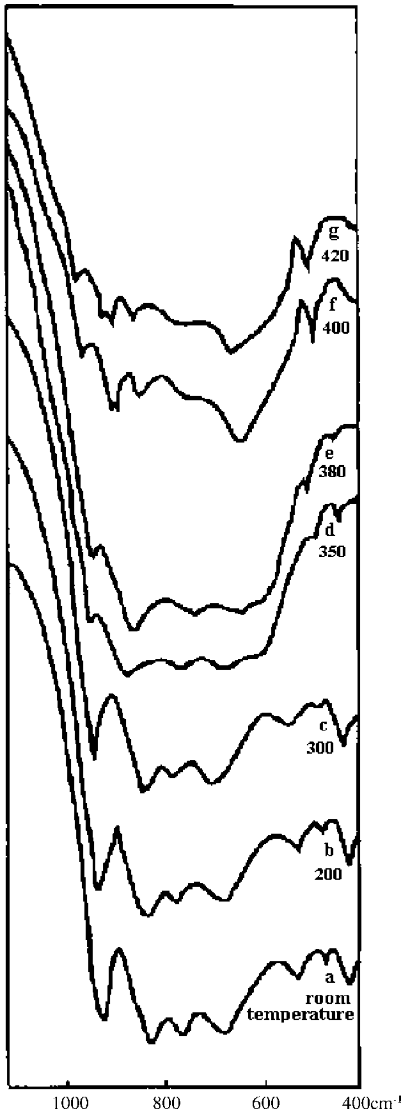

Fig. 3. IR spectra of $Sm(CuW_{11})_2$ at different temperatures.

characteristic peaks in the IR spectra of $Sm(CuW_{11})_2$ after heating for 30 min at 400 °C is greatly different from those of $Sm(CuW_{11})_2$ at room temperature. The resulting product, which is insoluble in water, suggests that $Sm(CuW_{11})_2$ has mainly decomposed. The exothermic peak at 412 °C in the TG-DTA curves is attributed to the crystallization of the decomposition product of $Sm(CuW_{11})_2$. Therefore, the decomposition temperature of $Sm(CuW_{11})_2$ is between 350 and 400 °C.

The following rules can be obtained from the data in Tables 1 and 2.

1. In the same series, the rare earth ternary heteropoly salts resemble each other in the thermal stability. The thermal stability of $Sm(CuW_{11})_2$ depends on the interaction between the rare earth metal ion and the ligand oxygen atoms, which can be determined by measuring the binding energy of inner electrons in the rare earth metal ion. The energy of $Ln_{3d5/2}$ in XPS is given in Table 3.

Table 2
The solubility in water of $Sm(CuW_{11})_2$ after treatment at different temperatures

T (°C)	Solubility
100	Soluble
200	Soluble
300	Soluble
320	Soluble
350	Some
380	Some
400	Insoluble
420	Insoluble

Table 3
Energy of $Ln_{3d5/2}$ in XPS

E (eV)	La	Nd	Sm	Gd	Dy
CrW_{11}		982.2	1083.1		153.6
MnW_{11}		982.7		143.9	
CuW_{11}	836.3		1082.9		153.9
$Ln(NO_3)_3$	836.5	983.8	1084.8	144.1	158.8

The results show that the increase of the negative charge of the anion causes to decrease the binding energy of inner electrons in the metal ion. With the same ligands but different Ln^{3+}, the bond energies of Ln–O show no obvious differences, therefore their thermal stabilities are quite similar.

2. In the same series, the thermal stability of ZMW_{11} varies with the element Z. The thermal stability of coordination compound ZMW_{11} (Z = Fe, Al and Ga) is higher than that of ZMW_{11} (Z = Co, Ni and Zn), indicating that the thermal stability increases with increasing charge of the cation of Z.
3. The order of the thermal stability of $Ln(MW_{11})_2$ is $Ln(FeW_{11})_2 > Ln(CoW_{11})_2 > Ln(CrW_{11})_2 > Ln(CuW_{11})_2 > Ln(MnW_{11})_2$. The order of the thermal stability of ZMW_{11} is $ZFeW_{11} > ZCoW_{11} > ZCrW_{11} > ZCuW_{11} \sim ZMnW_{11}$. The above relationships show that the main factor affecting the thermal stabilities of $Ln(MW_{11})_2$ and ZMW_{11} is the thermal stability of the ligand MW_{11}(M = Fe, Co, Cr, Cu and Mn) whose stability closely corresponds with that of the $MW_{12}O_{40}$ with Keggin structure [7].
4. The thermal stability of $Ln(MW_{11})_2$ or ZMW_{11} is higher than that of $MW_{12}O_{40}$ with Keggin structure [8]. The exothermic peak of $MW_{12}O_{40}$ in DTA curve is listed in Table 4.

Table 4
Temperature of exothermal peak of $MW_{12}O_{40}$ in DTA curve

$MW_{12}O_{40}$	*T* (°C)
$CrW_{12}O_{40}$	250
$MnW_{12}O_{40}$	250
$FeW_{12}O_{40}$	390
$CoW_{12}O_{40}$	320
$CuW_{12}O_{40}$	250

Occasional exceptions to this rule do occur, for example, in the water of a low pH, $MW_{12}O_{40}$ is more stable than $Ln(MW_{11})_2$.

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