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Der Chemica Sinica, 2013, 4(2):182-188



Synthesis and structural characterization of Tin (IV) Molybdotungstate-A Heteropolyacid Salt

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ABSTRACT

The present study focused on the structure elucidation of a new heteropolyacid salt named Tin (IV) molybdotungstate, synthesized at pH 1.0 using sol-gel method. Instrumental techniques like XRD, IR, TGA, SEM and EDS were used to elaborate the structural aspects. XRD studies exhibited that prepared sample was having amorphous structure. Infrared spectroscopy was used to investigate the functional groups and the active sites supporting the acidic character and SEM and EDS techniques described the elemental composition of the synthesized sample. Thermogravimetric technique indicated the weight loss rate due to dehydration and helps in ascertaining the number of water molecules. The structure derived on the basis of above analytical techniques gave an impression of the polyoxometallates structure embracing various functional groups, water molecules, acidic nature and ion exchange characteristics. Thus, SnMoW can also be used in electro-analytical analysis.

Keywords: Polyoxometallate, SnMoW, ion exchanger, Structure, heteropolyacids.

INTRODUCTION

Clearfield studied the inorganic ion exchangers, particularly heteropolyacid compounds and gave a pioneer step towards characterization and their applications and thus created a new area in the research world [1-3]. The general methods for the synthesis of the heteropolyacids are etherate, ion exchange, electro dialysis and precipitation.

Matkovic et al investigation demonstrated that the "ion exchange" methodology is suitable for the synthesis of phosphotungstic and molybdic acids in a high yield [4]. The heteropolyanion phase transfer chemistry was explained by M. T. Pope and gave a new beam of ray to the heteropoly compounds field [5-6]. These compounds are composed of complex network of MO_6 octahedra, the later having discrete fragments of metal oxide structures [7]. J.F. Keggin with the use of X-ray diffraction experimentally determined the structure of α -Keggin anions [8].

Mittal et al have synthesized some inorganic salts of tin possessing good ion-exchange characteristics and applied them as electro-active materials in various electro-analytical studies [9-13]. Besides the electro analytical studies heteropolyacid salts have been extensively used as catalysts for different industrial practice [14-15] to replace environmentally harmful liquid mineral catalysts [16]. We have synthesized some ion exchangers [17-19] and are excited to explore much more.

MATERIALS AND METHODS

Chemicals and Instruments

All the chemicals were of analytical grade. The basic materials like Tin chloride, sodium molybdate and sodium tungstate were procured from CDH chemical, India. Distilled water was prepared by double distillation plant. X-ray spectrum was obtained with an X-ray Diffractometer (Powder Method) - Panalytical.s X.Pert Procamera. Infrared studies were made with an IR- EFFINITY-21 CE Shimadzu spectrophotometer using the KBr pellet technique. TGA analysis were based on the changes observed in the synthesized material on Mettler Toledo Star System. SEM/EDS images were obtained by using EDS advanced microanalysis solution AMETAK electron microscope.

Preparation of Tin [IV] molybdotungstate [SnMoW]

The exchanger was prepared by adding Tin (IV) chloride (0.1M) to a continuously stirred aqueous mixture of sodium molybdate (0.1 M) and sodium tungstate (0.1 M) at 60°C in a volume ratio of 2:1:1 respectively. Gelatinous precipitates were obtained at pH 1.0. Gelatinous material was filtered and then washed with excess of DDW to wash out all the halide content. Precipitates were dried at 40°C and when the dried product was immersed in distilled water, it appeared into small granular morphology by absorbing water in its matrix. Then the granular material was further dried at 40°C to retain the water of crystallization and was kept in HCl (0.1 M), overnight to convert the material into the H⁺ form, with intermittent shaking and changing the acid. Precipitates were washed with DDW in order to remove excess acid and finally dried at 40° C. Various other conditions as given in table I were also tried to get the exchanger of desirable quality.

Table I: Preparation of SnMoW under different conditions.

Sample No.	Name of the constituents	Volume Ratio	Molar concentration	Temp	pH	IEC(meq/g)
1.	Tin chloride	2	1M	60°C	1.2	0.864
	Sodium tungstate	1	1M			
	Sodium molybdate	1	1M			
2.	Tin chloride	2	2M	55°C	1.8	0.554
	Sodium tungstate	1	1M			
	Sodium molybdate	1	1M			
3.	Tin chloride	1.5	1M	60°C	1.6	0.80
	Sodium tungstate	1	1M			
	Sodium molybdate	1	1M			
4.	Tin chloride	2	2M	65°C	1.2	0.734
	Sodium tungstate	1	1M			
	Sodium molybdate	1	1M			
5.	Tin chloride	1	1M	60°C	1.0	0.790
	Sodium tungstate	1	1M			
	Sodium molybdate	1	1M			

Ion-exchange Capacity

Column operation methodology was used to determine the ion-exchange capacity of the activated ion-exchanger, following the similar procedure as illustrated in the previous reports [18 -19].

Table II: Distribution coefficients (Kd) for different metal ions on Tin (IV) molybdotungstate

S.No.	Metal ion	Kd values
1.	Gd(III)	13.7
2.	Pr(III)	19.1
3.	Er(III)	22.6
4.	Sm(III)	14.6
5.	La(III)	13.9
6.	Ce(III)	22.3
7.	Tb(III)	3.8
8.	Y(III)	31.0

Sorption Studies

Distribution coefficient (Kd) values for the rare earth metal ions were determined by keeping 0.2g of the activated exchanger with 20 mL of different metal ion (0.01M) solutions to attain equilibrium, with intermittent shaking the

solution. The supernatant liquid was removed after 24 hours, to access the remaining metal ion concentration by EDTA titrations [21, 22]. Distribution coefficients values for different metal ions are given in the table II.

Regeneration of Ion exchanger

Exhausted exchanger was kept in hydrochloric acid (0.1 N), at least for 24 hours. After washing with DDW water, the ion exchange capacity was determined and this procedure was repeated many times to check the reproducibility. After five regenerations, ion exchanger loses 10% of its original capacity.

Infrared Spectra

Infrared spectra of SnMoW sample were recorded using KBr pellet medium and is depicted in the figure I. Four types of metal-oxygen linkages exhibit characteristics vibrational bands for structure elucidation in polyoxometalate chemistry.

- X-O-M, long and weak bond (4 internal oxygen connecting X-M),
- M-O-M (12 edge-sharing oxygen connecting M's),
- M-O-M (12 corner- sharing oxygen connecting M_3O_{13} units) and
- M-O, having almost double bond character (12 terminal oxygen bonding to one M atom).

FT-IR spectra of the samples in the region $1200-600\text{ cm}^{-1}$ is of interest as it explains the metal oxygen bonding in the heteropoly compounds [23].

Thermal Gravimetric Analysis

A TGA curve was obtained between 25°C and 800°C , with a constant heating rate of 10°C per minute, under nitrogen flow rate of 50.0 mL/minute. The number and nature of water molecules present in the HPA and thermal stability characteristics of the exchanger material can be interpreted on the basis of results shown in figure II.

X-Ray Diffraction

X-Ray analysis gives the information about the crystalline/amorphous content and size/orientation of crystallites. X-ray diffraction studies of Tin (IV) molybdotungstate were done by powder diffraction method and the observed pattern is given in figure III.

Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

Scanning electron microscopy reveals the information about the morphology and topography of the synthesized sample and the images of the sample were resolved by dispersing the powder on a double face conducting tape locked on a brass support. Pictorial representation of SEM is given in the figure IV.

RESULTS AND DISCUSSION

Tin (IV) molybdotungstate prepared by sol-gel method exhibits an ion exchange capacity of 0.864 meq/g. Out of various samples prepared, using different volume ratio, molar concentration, different pH and temperature conditions, sample no. 1 was picked up for further studies, since it shows maximum IEC. It is reproducible and shows maximum selectivity towards Y(III) as is evident from distribution coefficient studies. The exchanger can be regenerated over and over again, since it does not lose much of its ion exchange capacity even after five regenerations.

IR spectra of the SnMoW represents the following sharp and strong bands at:

1. Broad bands at 3291 cm^{-1} and 3048 cm^{-1} were due to stretching of -OH groups of the interstitial water molecules and W-OH (acidic) stretches.
2. A weak band at 2925 cm^{-1} was due to deformation vibration of the coordinated water molecules.
3. The strong and broad bands at $1787-1708\text{ cm}^{-1}$ gave the deformation vibration of interstitial water molecule.
4. Sharp band at $1519-1460$ and 1387 cm^{-1} were due to deformation vibrations of metal hydroxyl groups and interstitial water.
5. Sharp band at 1085 cm^{-1} was due to superposition of metal oxygen stretching vibrations.
6. A broad band at $889-525\text{ cm}^{-1}$ denoted the wagging, twisting and rocking modes of the water molecules.

Due to the coupling of valence electronic states with the vibrational modes of the molecules, the bands were either broadened or shifted from their normal modes. One important inference drawn from the bands that property of HPA/salts is their acidic behavior which is related to the presence of incorporated water.

From **EDS** studies, it is clear that elemental composition of the synthesized SnMoW exchanger contains the characteristics peaks of elements Sn, Mo and W. Atomic ratio of these elements was Sn:Mo:W—3.62:5.27:78.13 respectively .

Thermo gravimetric study solves the dilemma of the external water molecules which are consistent only up to 200°C. It is assumed that all the external water molecules are rooted up on heating the heteropolyacid compounds above than the recommended temperature. The number of external water molecules ‘n’ can be calculated by using Alberti formula [24], which is given as;

$$18 n = X (M+18 n) / 100 \dots\dots\dots (1)$$

where, X is % weight loss at 200°C, (M+18 n) is molecular weight of the material and n, the number of external water molecules. These losses follow the regular trend of inorganic ion exchangers. SnMoW experiences a weight loss of 10% up to a temperature of 200°C. By using the Alberti formula, the value of ‘n’ was found to be $33.53 \approx 34$. So, the empirical formula of the exchanger can be written as $[(\text{SnO}_2)(\text{H}_3\text{MoO}_3)_{1.4558}(\text{H}_3\text{WO}_4)_{21.5828}].34\text{H}_2\text{O}$ with a molecular weight 6027.096 a.m.u. This formula reveals relative ratio of different types of oxygen like molecular water, hydroxyl group and oxide in the synthesized material. A further weight loss of nearly 5.52% up to 500° C may be attributed to the dissipation/rearrangement of co-ordinate water hydroxyl groups and other functional groups.

X-ray powder diffraction studies reveal that there was no definite angle of diffraction line to tell about the crystallinity. Hence, the spectrum indicates their amorphous nature.

SEM image of Tin (IV) molybdotungstate explain that the particles were

- (i) broad in size range
- (ii) having an irregular shape
- (iii) no sign of crystalline structure and
- (iv) lack of clarity

These observations strongly gave a favor to their amorphous nature. Pictorial representation gave the evidence of linearly layered with little irregularity in the structure of SnMoW.

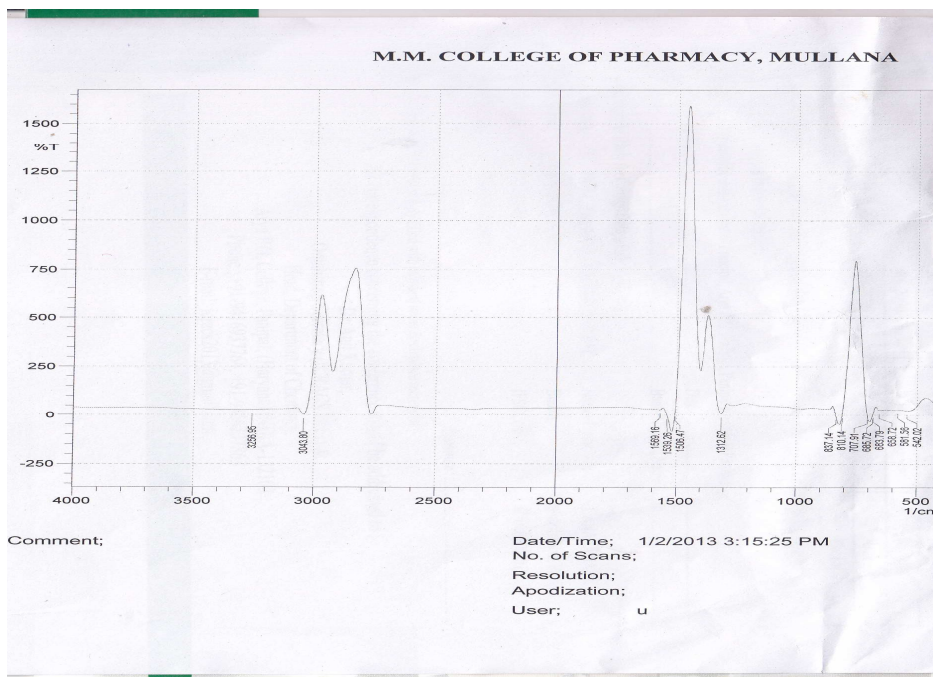


Figure I: IR spectrum of tin (IV) molybdotungstate

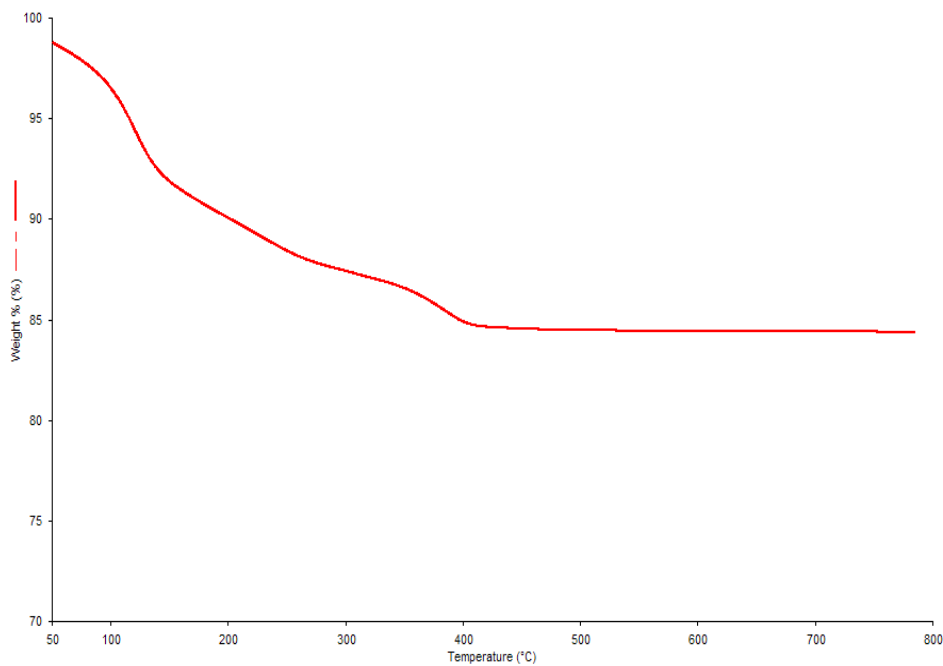


Figure II: TGA curve of SnMoW

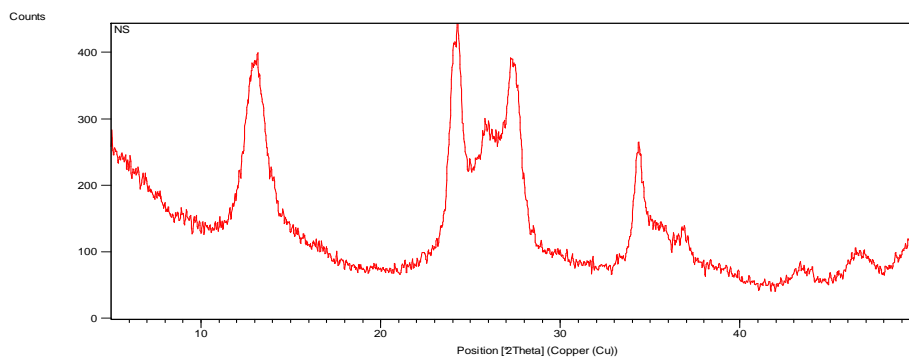


Figure III: X-ray diffraction pattern of SnMoW

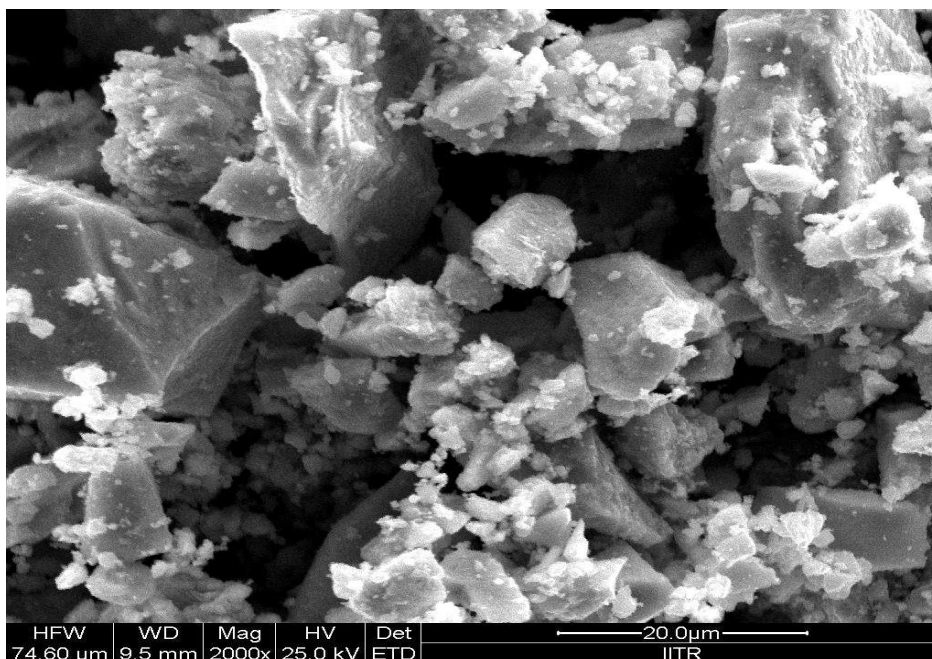


Figure IV: SEM images of a sample of SnMoW

Application as Ion-selective Electrode

It was observed that Tin (IV) molybdotungstate expressed different selectivities towards different metal ions. But maximum response behavior was observed towards Y(III) ions over other rare earth metal ions. Thus, this electro-active material can be used as an electro-active component in the preparation of heterogeneous solid membrane electrodes sensitive for Y(III) ions.

CONCLUSION

In the present study, an acidic and reproducible Tin [IV] molybdotungstate has been introduced as an heteropolyacid salt. The salt has been synthesized using ion exchange method. Structural aspects were deduced on the basis of instrumental techniques like FTIR, X-ray diffraction, TGA, SEM and EDS analysis. On the basis of above analysis the empirical formula of the amorphous SnMoW products was formulated as $[(\text{SnO}_2)(\text{H}_3\text{MoO}_3)_{1.4558}(\text{H}_3\text{WO}_4)_{21.5828}]\cdot 34\text{H}_2\text{O}$ with a molecular weight 6027.096 a.m.u. Thus, SnMoW have been identified a polyoxometallate having defected lacunary geometry and can also be applied as electro-active materials.

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