NOVEL HETEROPOLYACID SALT: TITANIUM (IV) MOLYBDOTUNGSTATE

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ABSTRACT

The present investigation describes the geometry of an original compound, Titanium (IV) molybdotungstate [TiMoW] prepared by using the ion-exchange route. To elaborate the structural aspects various analytical techniques were employed. The amorphous behavior of the compound was established using XRD. Infrared spectroscopy was used to assign dynamic sites responsible for acidic characteristics of the sample. SEM/EDS has been used to describe the composition of elements present in the prepared sample. Thermogravimetric techniques indicated the weight loss rate and helped in ascertaining the number of water molecules. Thereafter, the derived structure furnished a geometry of heteropolyacid salt, embedded with acidic and ion exchange characteristics.

Keywords: Titanium Molybdotungstate, Synthesis, Heteropolyacid, Ion-exchange, IR.

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INTRODUCTION

Heteropolyacid salts act as promising ion exchangers for the detection and estimation of metal ions and also as efficient catalysts for organic synthesis. Besides these major applications, these complex compounds can be used in analysis, histology and also as a dynamic component of many reagents like *Folin-Ciocalteu* reagent and *folins phenol* etc. Keggin has formulated the structural aspects of α -Keggin anions using an X-ray diffraction pattern.¹ Later on, M.T. Pope extended the structural aspects of these compounds and suggested that the fundamental unit comprises of setting up of MO_6 octahedral having fragments of metal oxide structures.² W Grace³ synthesized titanium arsenate which is selective for a number of ions such as Ba^{2+} , Sr^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+} , Pb^{2+} . Qureshi and his co-workers synthesized a series of titanium-based isopolyacid salts; titanium tungstate, titanium molybdenite, titanium antimonite which are used to separate the alkali metal ions and titanium selenite was used as Cd^{2+} selective ion exchanger.⁴⁻⁷ Titanium vanadate synthesized at various pH (10, 6.8, 4.8, and 2.7) and exchanger having 0.65 meq/g ion-exchange capacity was used for binary mixtures separation of Sr^{+2} with Ba^{2+} , Ca^{2+} and Mg^{+2} while titanium silicate was used for the separation of transition metal ions.⁸⁻⁹ L. Szirtes and L. Zsinka prepared amorphous titanium tellurate.¹⁰ Sharma et al studied the chromatographic behavior of 40 metal ions using titanium-based ion exchanger.¹¹ This property can be useful for the estimation of environmentally hazardous¹² ions. Most of these salts were selective for more than one metal ion and were employed for chromatographic separation of generally binary mixtures. Thus, their use as a sensor cannot give the utmost consistency, which is the vital requirement for the estimation of any metal ion and then an era of double salts of heteropolyacids came into limelight and frequent augmentation was observed in this field. This field has provided a zenith for researchers. The crystalline phase of titanium (IV) tungstosilicate having 0.44 meq/g IEC was prepared by Siddiqi and Pathania by adding solutions of tungstosilicic acid with alcoholic solution of titanium (IV) chloride and then employed for the separation of ions using column operation methodology.¹³ Titanium arsenosilicate was prepared by Varshney et al.¹⁴ Ahmad et al synthesized Titanium tungstophosphate immobilized on silica and employed it for the removal of lanthanum.¹⁵ Yaveri et al synthesized and studied analytical application of Titanium (IV) molybdophosphate.¹⁶ A lead selective exchanger named Titanium aluminum silicate was assembled by

Sun et al.¹⁷ Kuznicki et al synthesized amorphous heteropolyacid salt named titanium phosphosilicate.¹⁸ Srivastava and his co-fellows synthesized titanium tungstoarsenate possessing 0.86 mequiv. g⁻¹ ion exchange capacity.¹⁹ Recently, a composite membrane based on sulfonated polysulfone-natural zeolite-titanium dioxide has been prepared.²⁰ Most of the above-mentioned reports contain molybdate, titanates and tungstate in the separate heteropoly compounds, but we have incorporated successfully all the three moieties in a single complex showing heteropoly compound characteristics and some of our successful efforts in this field are shown in references.²¹⁻²⁵ The work presented in this manuscript depicts the synthesis and characterization of a novel compound named TiMoW.

EXPERIMENTAL

Material and Methods

Essential metal ion solutions were prepared by weighing reagents of utmost purity i.e. greater than 99%. Standardization was carried out, wherever required. IR studies of TiMoW were carried out with an instrument having specification as "Perkin, ABB spectrophotometer" (resolution > 0.7 cm⁻¹) by impregnating in KBr pellet. X-ray powder analysis of the compound was done with Rigaku Dmax III C instrument. TGA analysis was done on Mettler Toledo Star System with a limited deviation of ± 0.25 K and the temperature precision is up to ± 0.15 K. SEM/EDS of synthesized material was performed with JEOL (JSM 6510LV) instrument.

Preparation of Titanium [IV] Molybdotungstate [TiMoW]

Different samples of TiMoW were prepared by slow addition of titanium (IV) chloride solution to a constantly stirred aqueous solution of sodium molybdate and sodium tungstate (high purity, procured from CDH chemicals/Merck chemicals) under variable conditions as mentioned in the table 1. Sticky silvery light precipitates were obtained, which were digested for 3 hours to get pure and superior quality exchanger. Then, the precipitates were separated from an excess of chloride ion by frequently washing with DDW and then again dried at 40°C. Subsequently, the material was converted to granular form by immersing in DDW. The material was transformed into active species i.e. H⁺ form. The activated form was excessively washed with water to get rid of the excess of sticky acid and finally, the samples were again dried at low temperature i.e. 40°C. Different preparatory conditions (given in Table-1) were tried and sample no. 1 was picked up for further investigations, as this is comparatively better ion exchanger because of maximum IEC.

Physicochemical Characterization

Ion Exchange Capacity (IEC)

To determine IEC of the sample, column operation methodology was employed as mentioned in the previous communications.²¹⁻²⁵

Distribution Coefficient Studies (Kd)

Distribution coefficients (Kd) for various metal ions were calculated by following the same strategy and formula as described in previous reports.²¹⁻²⁵ Results are summarized in Table-2.

Structural Characterization

Infrared Spectra

Metal-oxygen linkages exhibit a variety of characteristic vibrational bands to elucidate polyoxometalate chemistry.

- internal oxygen connecting X-M,
- edge-sharing oxygen connecting M's,
- corner-sharing oxygen connecting M₃O₁₃ units and
- terminal metal-oxygen bonding.

FTIR spectra in the region 1200–600 cm⁻¹ explain M-O bonding pattern in the heteropoly compounds^{26, 27} and FTIR findings of the compound are plotted in Fig.-1.

Table-1: Optimization of Preparatory Conditions of TiMoW.

Sample No.	Respective Ingredients	Volume Ratio	Molar Concentration	Temp ($^{\circ}\text{C}$)	pH	IEC (meq/g)
1.	TiCl_4	2	1	60	1.0	0.982
	Na_2WO_4	1	1			
	Na_2MoO_4	1	1			
2.	TiCl_4	2	2	55	1.8	0.664
	Na_2WO_4	1	1			
	Na_2MoO_4	1	1			
3.	TiCl_4	1.5	1	60	1.6	0.845
	Na_2WO_4	1	1			
	Na_2MoO_4	1	1			
4.	TiCl_4	2	2	65	1.2	0.878
	Na_2WO_4	1	1			
	Na_2MoO_4	1	1			
5.	TiCl_4	1	1	60	1.2	0.975
	Na_2WO_4	1	1			
	Na_2MoO_4	1	1

Fig.-1: FTIR Spectrum of TiMoW

Fig.-2: TGA Behavior of TiMoW

Table-2: K_d Values for Various Metal Ions

Rare Earth Metal Ion	Gd(III)	Pr(III)	Er(III)	Sm(III)	La(III)	Ce(III)	Eu(III)	Tb(III)	Y(III)
K_d	16.7	17.7	22.6	8.0	8.9	33.5	14.0	9.0	37.8

Fig.-3: X-ray Diffraction Pattern

Fig.-4: SEM Image

Thermal Analysis

A TGA curve of the sample is symbolized in Fig.-2.

X-Ray Diffraction

The resultant pattern of XRD analysis of TiMoW is shown in Fig.-3.

Scanning Electron Microscopy and Energy Dispersive Spectroscopy [SEM and EDS]

SEM images of the prepared compound are shown in Fig.-4.

RESULTS AND DISCUSSION

Ion-exchange Capacity

Out of various samples synthesized under different conditions, IEC of the superior sample (1) was deduced as $0.98 \pm 0.02 \text{ meq g}^{-1}$. Sample 1 is highly selective for Y(III), as it is evident from Kd values.

Instrumental Characterization

Results of FTIR of TiMoW confirmed different bands present in the compound corresponding to heteropoly compounds.

The broad peak at 3625 cm^{-1} , weak band at 2921 cm^{-1} , sharp band at 1740 corresponds to various stretching and bending modes of the interstitial water molecule, whereas sharp band at 1393 cm^{-1} and broadband at $985\text{-}675 \text{ cm}^{-1}$ represents stretching and bending mode of metal-oxygen bonds.

Coupling of electronic states and vibration of the molecules broadened or moved the bands from their normal modes.

Electron diffraction spectra of TiMoW shows the atomic ratio of various elements in the compound Ti:Mo:W:O::19.64:18.75:27.10:34.52, respectively. Thus, various calculations give the empirical formula of the synthesized exchanger as $[(\text{TiO}_2)_{1.047}(\text{H}_3\text{MoO}_3)(\text{H}_3\text{WO}_4)_{1.445}] \cdot n\text{H}_2\text{O}$

Thermal Analysis indicated that TiMoW loses 8.5% of weight up to a temperature of 200°C. This weight loss pattern assisted in the estimation of number of water molecules 'n' by using Alberti formula:²⁸

$$18n = X(M + 18n) / 100$$

This gives the value of 'n' as $2.959 \approx 3$. Empirical formula of the exchanger can be written as $[(\text{TiO}_2)_{1.047}(\text{H}_3\text{MoO}_3)(\text{H}_3\text{WO}_4)_{1.445}] \cdot 3\text{H}_2\text{O}$ with a molecular weight 627.349.

As the coordinated water molecule gets escaped and also there is a rearrangement of functional groups so further weight loss of 5.52% was observed up to 500°C.

X-ray powder pattern of TiMoW is shown in Fig.-3 and the studies revealed that there was no definite angle of diffraction to tell about crystalline behavior, therefore, the amorphous nature of the compound is confirmed.

SEM images (Fig.-4) of titanium (IV) molybdotungstate explained that the particles are broad, having uneven contour, lacking crystallinity and clarity. These observations strongly favor amorphous nature with a linearly layered structure with little irregularity.

The present investigation depicts the complete structural information of this amorphous compound having empirical formula $[(\text{TiO}_2)_{1.047}(\text{H}_3\text{MoO}_3)(\text{H}_3\text{WO}_4)_{1.445}] \cdot 3\text{H}_2\text{O}$ with a molecular weight 627.349.

Applications as Ion-selective Electrode

On the basis of distribution coefficient values, it was conferred that Titanium (IV) molybdotungstate exhibited excellent selectivity towards Y(III) ions over other metal ions employed in the analysis. Thus, the prepared material can act as an effective electro-active component in the preparation of a sensor membrane and electrode sensitive for Y(III) ions.

CONCLUSION

A novel Heteropolyacid salt: titanium [IV] molybdotungstate has been synthesized under different reaction conditions and then structural analysis was done using different analytical and instrumental techniques. This analysis helps in formulation of empirical formula of the derived amorphous TiMoW product is $[(\text{TiO}_2)_{1.047}(\text{H}_3\text{MoO}_3)(\text{H}_3\text{WO}_4)_{1.445}] \cdot 3\text{H}_2\text{O}$ with a molecular weight 627.349 a.m.u. Thus, TiMoW has been identified as polyoxometallates selective for Y(III) species.

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