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Hydrothermal Synthesis of a New Anderson Type Molybdenum based Polyoxometalates (POMs)

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Abstract: Polyoxometalates (POM) or poly metal oxide Anderson type compound $Na_{12}[NiVMo_5O_{24}].11H_2O$ has been synthesized under hydrothermal conditions. The compound is formed at the pH of 4.36 with CH_3COOH-CH_3COONa as a buffer. Light green big crystals were evolved after some days and are characterized using ICPAES for elemental analysis, IR Spectroscopy for M-O and M-O-M vibration frequency, TG- DTA for Thermal stability of the said compound and SEM for morphological study of the compound.
Molecular weight of the compound is determined by the cryoscopic method which has found to be little lesser than the calculated value.
Key words: Anderson type, Hydrothermal synthesis, Molybdenum, SEM.

Introduction

Polyoxometalates (POMs) is large class of nanosized metal oxygen cluster of oxo-complex anions supported by transition metals. These inorganic compounds have become a chapter of especial focus due to their intrinsic and unique properties regarding metal oxide surfaces and abundant topologies. Nowadays, they are largely employed as a prominent catalyst in various chemical reactions and a potential substitute in medicine, photochemistry electrochemistry and magnetism[1-3].

These compounds are self assembly of metal ligated oxo anions in a cluster which enables the size, shapes alteration to achieve the targeted product[4].

However, it is very interesting to note that Polyoxometalates have showed its presence due to their large number and variety [5].

Hundreds years have passed since the development of Polyoxometalates chemistry took place, the research for the knowhow of construction of these smart materials and their way of action is going on. The numerous structural macromolecules of Keggin, Dawson or Lindquist type have established. Much work has not been done over the structure and working of Anderson type polyoxometalates.

Anderson type Polyoxometalates show planar type of structure. Each addenda atom (Mo) has two terminal oxygen atoms making them highly reactive and also enables them to attach with other transition metals[6].

In the present piece of work, synthesis and characterization of Anderson type Transition metal substituted Polyoxometalates has been carried out in hydrothermal process.

Experimental

Analytical reagents used were of laboratory grade. Magnetic stirrer was employed under controlled temperature for preparing the aqueous solution of the reagents. The solutions were prepared freshly by dissolving the requisite amount of reagents in distilled water. The starting pH of the solution was maintained by the EI digital pH meter.

The elemental analyses of nickel, vanadium, molybdenum and sodium metal present in the compound were carried out by using inductively coupled plasma atomic emission spectroscopy(ICPAES), (make Jobin Yvon France of model JY Ultima-2) at IIT Powai, Mumbai. The IR spectra were recorded by Perkin Elmer 577 spectrophotometer in the region 4400-450 cm^{-1}. The thermal studies of the polyoxometalates were carried out by heating them between 25-940 ºC at 10 ºC/min using Perker-Elmer USA of model Diamond TG-DTA followed by solubility determination. The apparent molecular weight of the sodium salts were determined cryoscopically using Beckmann's thermometer.

Synthesis of 5-Molybdovanadonickelate (II) anion

1.95 gm of Nickel Chloride was dissolved in 30 mL water to prepare 8.2 mmol solution. 8.2mmol solution of sodium vanadate was prepared by dissolving 1g in 40 mL of water. Both the solution were mixed with each other followed by addition of 10 mL of acetic acid in order to maintain acidic condition[7-8] of the solution

The above mixture is finally added dropwise to the 40.99mmol solution of Sodium Molybdate till the solution reaches to a constant pH, in this case it was 4.2.A buffer solution was added to maintain the respective pH of the solution **(Fig-1)** .The ultimate or resulting solution was taken into stainless steel autoclave for the hydrothermal synthesis. After 4 days light green crystals were separated, washed with n-hexane and kept for analysis.

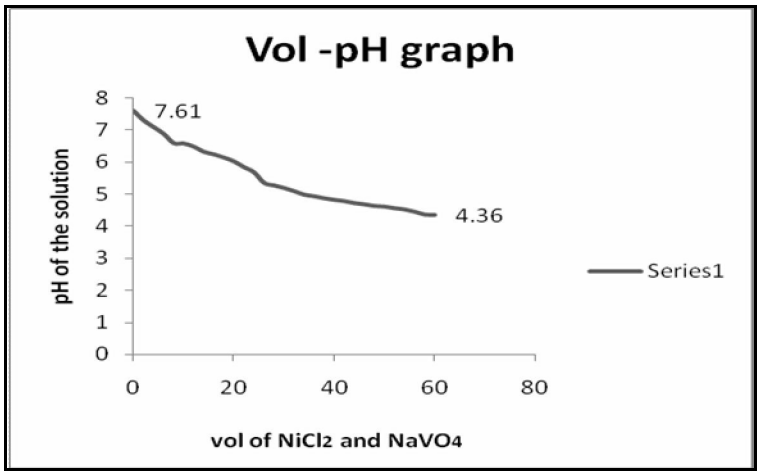

Fig- 1: Volume-pH curve plotted with pH meter during addition of aqueous solution of addenda with aqueous solutions of heteroatom

Result and discussion

The synthesized Molybdenum based Anderson type compound is Na_{12} $[NiVMo_5O_{24}].11H_2O$.
It comprises of $NiCl_2$, $NaVO_4$ and $NaMoO_4$ in stoichiometric ratio.
The Poly Metal Oxide compound oozed out in good yield at the final stage of its synthesis and is based upon the formula $[XX'M_5O_{24}]^{n-}$ where X and X' are the heteroatoms and M is the addenda.

ICPAES

The observed elemental analysis as found from the ICPAES analyser are
Exp: Ni: 4.1, V: 3.5, Mo: 33.6 and Na: 18.1
Calc: Ni: 4.11, V: 3.49, Mo: 33.59, Na: 18.08
The above result supported the formulation of the empirical formula of the compound.

TG-DT A

The TG curve **(Fig 2)** of the compound shows weight loss of the compounds in two steps. The first weight loss is 12.94% from 25^0C to 110^0C.The second weight loss of the compound is 9.04% from 110^0C to 940^0C.Both the weight loss attributes for the disintegration of the coordination water molecules of the compound.

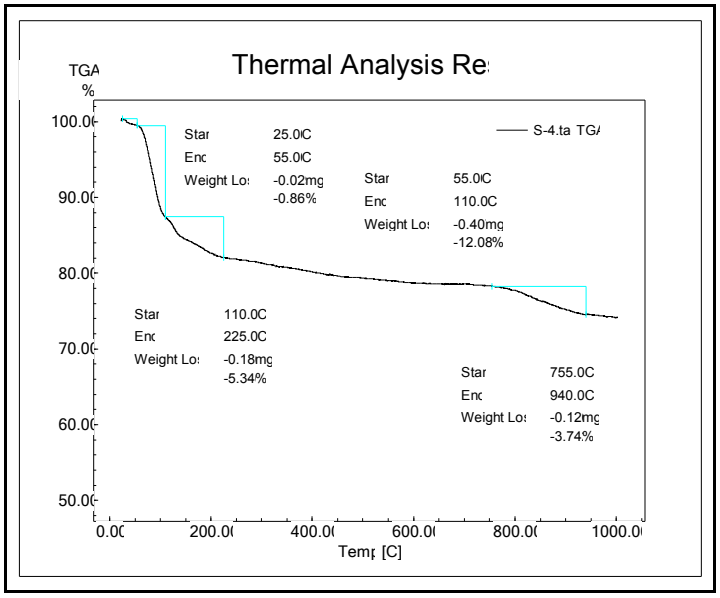

Fig- 2: Shows the loss in weight of the POMs during its thermal treatment from temp range of 25^oC to 940^oC

IR analysis

The IR spectrum (IR Fig 3) of the compound shows very broad characteristic peaks of 3514 cm^{1-} for water molecule. This is assigned to O-H stretch peak indicating the presence of lattice water molecules.

781cm^{-1} and 895cm^{-1} shows Mo-O_t and Mo-O_b stretching vibration[9].632cm^{-1} depicted Mo-O_b-Mo vibration in the compound. Further, 929,1639,1803,2129 cm^{-1} showed the presence of Anderson type compound in the structure[10].

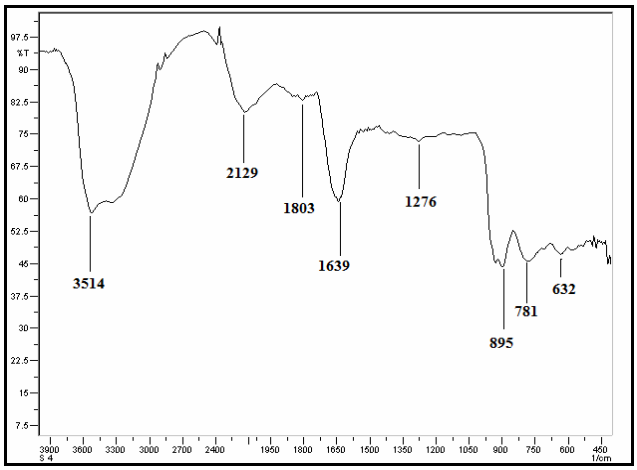

Fig 3 Shows the bond vibration of M-O and M-O-M in the polyoxometalates

SEM

The SEM micrographs of compound **(Fig 4)** featured a mixture of small crystals with few big crystals. The micrographs also suggested that the large particles were observed possibly due to the polyoxometalates present in the salt of the metal oxide which was responsible mainly for the Anderson structure. An array of uniform small crystals were observed with few sparse areas in these micrographs.

The embedded particles were spherical in shape having the size of 2-4µm. These micrographs suggested more uniform crystal sizes with few large crystals. The large particles would actually be aggregates of independent crystals of considerably smaller size.

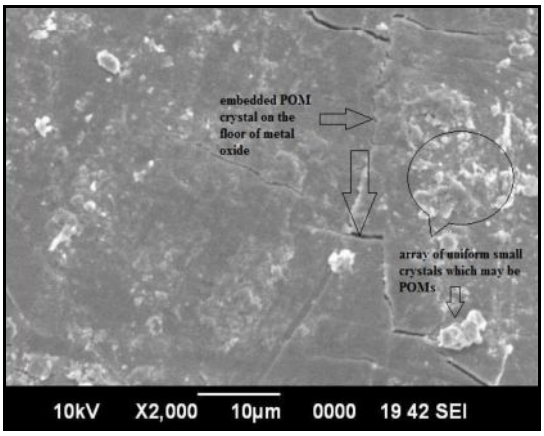

Fig 4-SEM showing morphological view of the compound.

Cryoscopic method for the molecular weight determination

The cryoscopic method has been used for the determination of average molecular weight of the polymeric compounds[11-12].P.Shoemaker et.al[13] and M.T.Pope and co-worker[14] determined the molecular weight of polyoxometalates cryoscopically with a little modification using sodium sulphate decahydrate and water as the solvent. The depression in freezing point is calculated by the graphical method and molecular weight by putting the value of ΔT in the formula

$$M = \frac{1000 k_f X}{W \cdot \Delta T}$$ where,

M= Molecular weight of the solute.
X= Weight of solute in gm.
W= Weight of solvent in gm.
ΔT=Depression in freezing point.

K_f= Molal depression constant.
$= \frac{0.002T^2}{L}$
Where T=Freezing point of solvent
L= Latent heat of fusion.)
is applied to find the molecular weight of the compound.
The molecular weight of the compound has been found to be 1350, calc is 1429.2.

Conclusion

Sodium salt of 5-molybdo heteropoly oxometalate has been synthesized under hydrothermal condition and is characterized by spectroscopic methods. The elemental analysis shows 1:1:5 atomic ratio of heteroatom with addenda agrees with the established formula of the Anderson type POMs. Deviations have been observed in IR Spectroscopy with that from Keggin anion.

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