

# Synthesis and Characterization of Keggin type Phosphotungstic Heteropoly acid and catalytic activity in Conversion of Trihydric alcohol into Acrolein

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**Abstract**—Keggin type of heteropoly acids such as phosphotungstic acid (HPW) was synthesized from its precursor solution. Synthesized HPW was characterized by FT-IR and XRD technique which reveals that the formation of HPW anions and also crystallinity respectively. The synthesized solid catalyst was evaluated for its catalytic activity for dehydration of trihydric alcohol to form acrolein. Catalytic reaction was monitored by TLC and the resultant product were analyzed by UV-visible spectrophotometer, FT-IR spectrum and Nuclear Magnetic Resonance Spectroscopy (NMR).

**Keywords:** Heteropoly acids; catalyst; phosphotungstate; trihydric alcohol; acrolein

## I. INTRODUCTION

The impact of chemicals on environment has been recognized and adopting cleaner technology for conversion of organic compounds into valuable commodity chemicals is important. Conventional mineral acids are homogeneous and corrosive in nature. Disadvantages of homogeneous catalysts have raised an attention towards heterogeneous catalysts. Replacement of hazardous chemicals by developing newer methods with environmentally benign chemicals is a major step and this forms the major platform for green chemistry.

Heteropoly acids (HPA) are transition metal oxygen anion clusters having metal-oxygen octahedral as a basic structure. They are represented by the general formula  $[X_xM_mO_y]$ , 'X' being a hetero atom with co-ordination number +3 or +4 (P, Si, B, Al, Ge and As), 'M' is a addenda atom having co-ordination number +5 or +6 (Mo, W, V, Ta, Nb, Os) and are attached to hetero atoms through oxygen atoms (1-2). They deserve special attention due to their unique physicochemical properties in catalyzing reversible redox reactions, thermally stable, high bronsted acidity determined by Hammett acidity function (1-2), less corrosive and more importantly easy regeneration. They have discrete mobile ionic structure. Keggin type of HPA is widely employed in reactions and is of prime important in catalysis is due to its stability, selectivity and efficient both in reactivity and acidity (3-6). They are soluble in polar solvents and insoluble in non-polar solvents. Hence the important properties of HPA relevant to catalysis have been utilized and its application has been evaluated.

The present investigation focuses on the synthesis of phosphotungstic acid ( $H_3PW_{12}O_{40}$ ) and characterization by FT-IR spectroscopy and XRD techniques to reveal the presence of HPW. Synthesized HPW catalyst was tested for its catalytic activity in dehydration of trihydric alcohol. The resultant product was analyzed by UV-visible spectrophotometer, thin layer chromatography and NMR spectroscopy. The results were tabulated and discussed in detail.

## II. EXPERIMENTAL METHODS

### Materials and Reagents

$Na_2WO_4$  (99.9% purity) purchased from Sigma Aldrich, HCl (35%),  $H_3PO_4$  (88% purity), Glycerol (99%),  $CDCl_3$ , Ethyl acetate (99.5%) from Himedia, Hexane (99.9%) from Merck, Diethyl ether (99%) from qualigens and distilled water was used throughout the reaction.

### Preparation of Phosphotungstic acid ( $H_3PW_{12}O_{40}$ )

$H_3PW_{12}O_{40}$  was synthesized by the addition of sodium tungstate 10gm in  $H_2O$  to a solution of 1ml of  $H_3PO_4$  (85%). The solution was stirred and heated to boiling point followed by addition of conc. HCl. The catalyst was extracted with ether. Subsequent addition of ether was followed and the lowest layer which is perfectly clear is transferred to a beaker and dried (7-8).

The mechanism and stoichiometric equation for synthesis of HPW is given below.



### III. CHARACTERIZATION OF HPW

Synthesized HPW was characterized by FTIR spectroscopy and X-ray diffraction. FTIR was recorded on a Shimadzu FTIR 8000 series Spectrometer (Kyoto, Japan); by disc plate method using KBr pellets. X-ray diffraction patterns were performed on an XRD 7000. NMR spectra were recorded using a Bruker 400-MHz FT-NMR spectrometer (Karlsruhe, Germany). Samples were dissolved in CDCl<sub>3</sub>, and Tetra methyl silane was used as an internal standard for the measurement of NMR.

#### Results and Discussions

##### Fourier Transform Infrared Spectroscopy (FTIR)

The FT-IR spectrum of HPW is given in Fig.1. The absorption peak for phosphorous bonding with oxygen (P-O) appears at 1017cm<sup>-1</sup>, whereas peak at 977.58 cm<sup>-1</sup> denotes metal oxygen bond (W-O), peak at 921.79 cm<sup>-1</sup> denotes metal oxygen metal bridged (W-O<sub>b</sub>-W) and peak at 800.36 cm<sup>-1</sup> corresponds metal oxygen metal (W-O<sub>c</sub>-W).

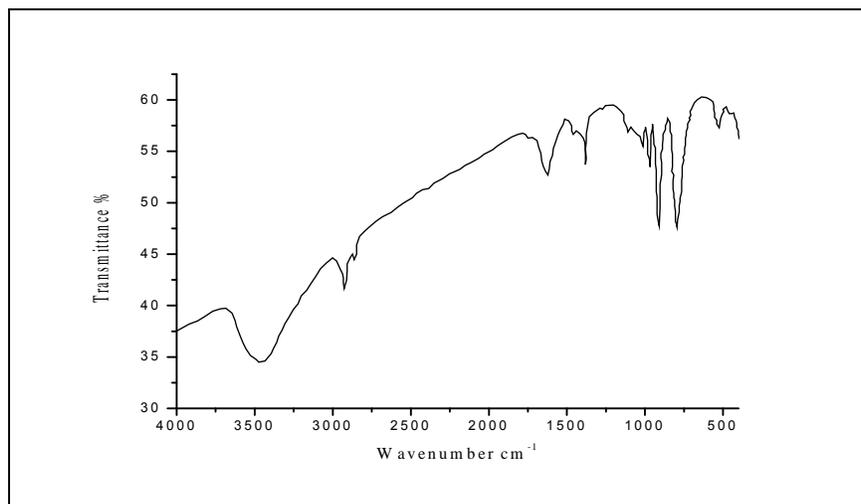


Fig.1. FT-IR spectra of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>

##### X-ray diffraction of the HPW catalysts Equations

X-ray diffraction patterns were performed on an XRD 7000 using Cu K $\alpha$  radiation with a wavelength of 1.54 nm to detect the crystal structure of the HPA's. Sharp peaks indicate the crystallinity of the catalyst. The crystal size was determined using the Scherrer's equation [10]. X-ray diffraction pattern of HPW is given in Fig.2.

Glycerol (1,2,3-propanetriol or glycerine) is a trihydric alcohol which has two primary hydroxyl groups and one secondary hydroxyl group and highly functionalized molecule. It can readily undergo oxidation, reduction, dehydration, oligomerisation, esterification, etherification etc., yielding numerous promising chemicals.

Synthesized solid acid catalyst was evaluated for its catalytic activity by dehydration of glycerol to acrolein. In a two-necked round bottomed flask (100 mL) equipped with a water-cooler condenser, a thermometer and a magnetic stirrer substrate and the catalyst was added in a mole ratio of (1:1) and heated at 240<sup>o</sup>C. Progress of the reaction is monitored by withdrawing samples at different intervals of time and analyzing through thin layer chromatography using ethyl acetate and hexane as solvents in the ratio (1:9) respectively. Complete conversion of alcohol to acrolein takes place after 60 min. Further the product was separated by extraction process using ethyl acetate as solvent and excess water was removed by addition of sodium sulfate. Reactants and products were characterized by UV-Visible spectrophotometer, FT-IR spectroscopy, <sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance (NMR) spectroscopy.

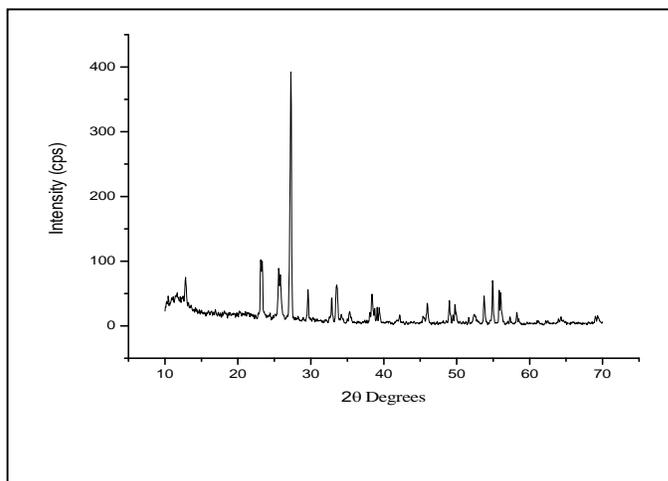


Fig.2. XRD pattern of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>

#### IV. CATALYTIC ACTIVITY

##### *Results and Discussion*

##### *UV-Visible Spectrum*

Sample was analyzed by UV-Visible spectrophotometer in the wavelength of 200-400 nm using ethyl acetate as reference sample. Appearance of absorption peaks observed at 251, 275, 399, 736nm. The absorption peaks from 200nm - 400nm corresponds to unsaturated carbonyl group and presence of bands 251,275 and 399nm observed in these range indicates the presence of carbonyl group which is shown in Fig.3

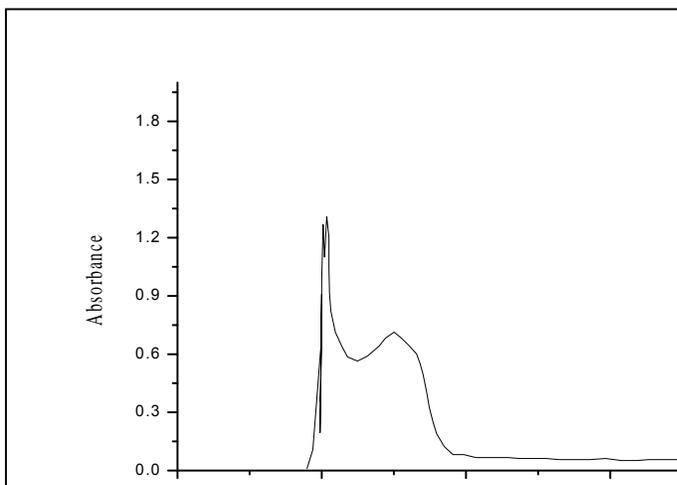


Fig.3. UV-visible spectrum of acrolein

#### Fourier Transform Infrared Spectroscopy (FT-IR)

IR spectrum of the sample shows the C=O stretching frequency at 1792-1742 cm<sup>-1</sup> and C=C stretching frequency at 1683-1602 cm<sup>-1</sup> and -OH peak appears at 3404 cm<sup>-1</sup>. The FTIR spectrum of the product is given in Fig.4

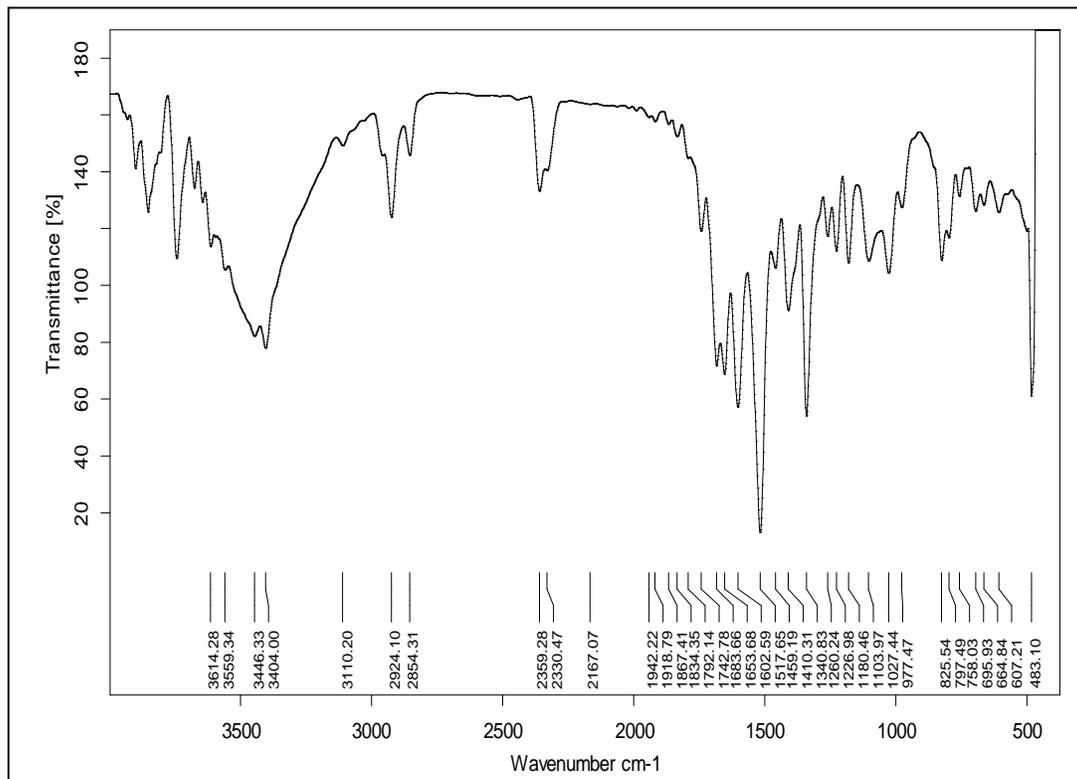


Fig.4. FT-IR spectra of Acrolein

#### Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear Magnetic Resonance spectroscopy for the sample was carried on using Bruker-400 spectrometer with CDCl<sub>3</sub> as an internal standard. A triplet was observed at a value of 0.8 at an intensity of 3.03 which is characteristic of methyl protons adjacent to methylene protons. A quartet was observed at a value of 3.68-3.63 which is characteristic of methylene protons adjacent to methyl protons depicted in figure (5). <sup>13</sup>C NMR predicts the number of carbon atoms and the values were given further. The value of  $\delta$  at 13, 19, 59 and 168 ppm corresponds to number of carbon atoms shown in Fig.6

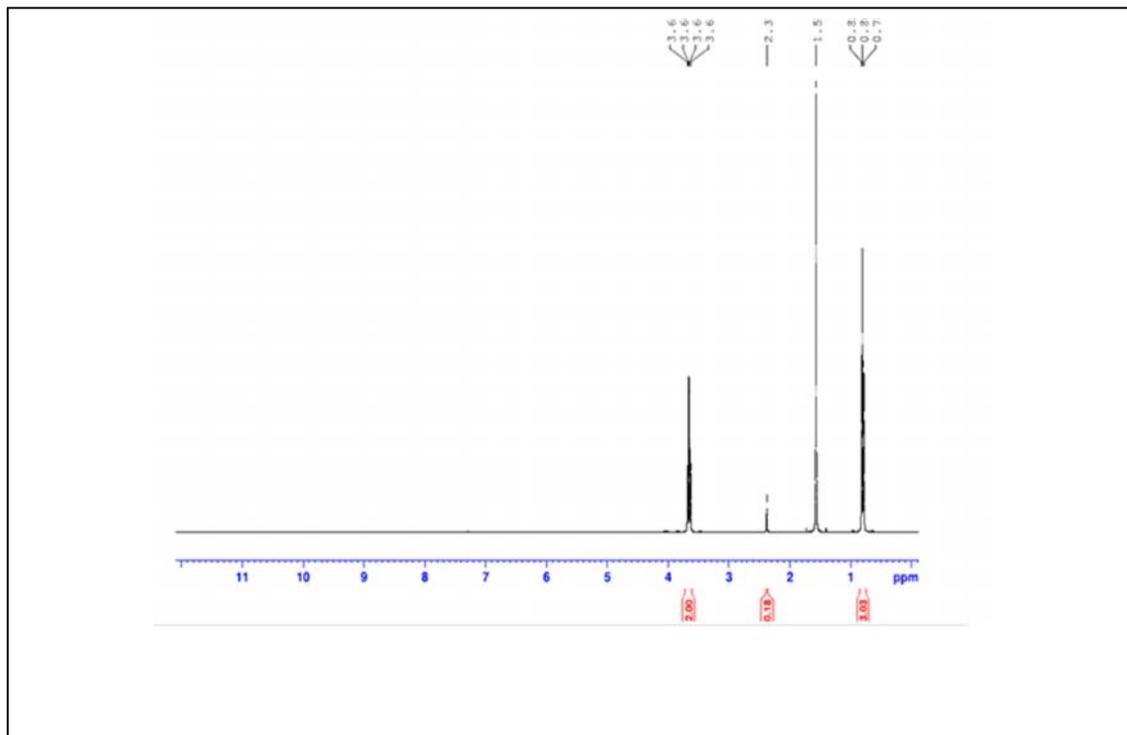


Fig.5. <sup>1</sup>H NMR spectrum of Acrolein

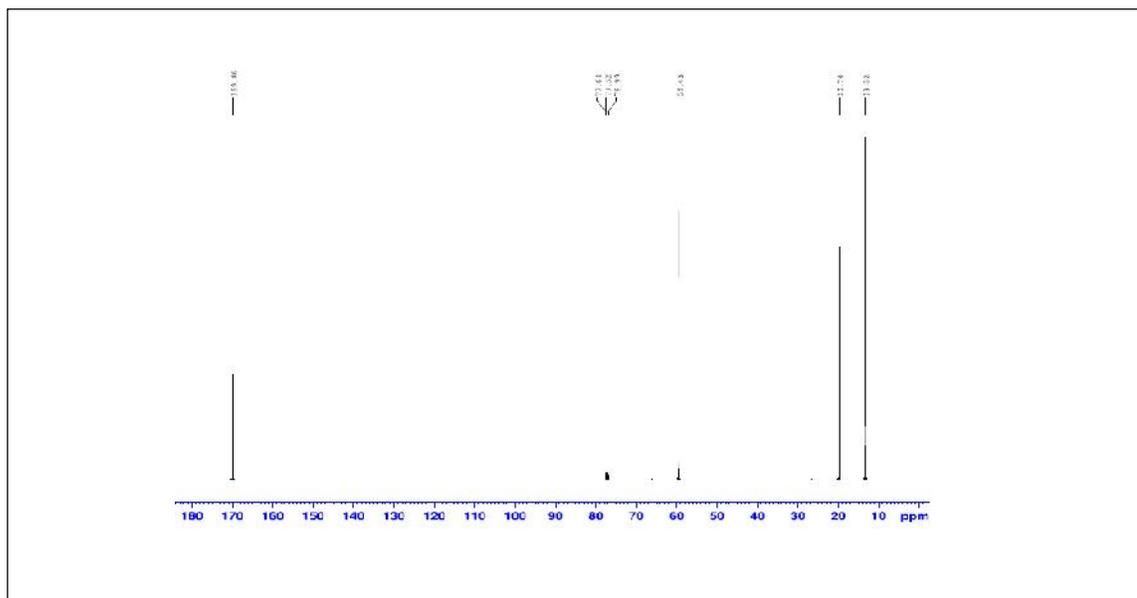


Fig.6. <sup>13</sup>C NMR spectrum of Acrolein

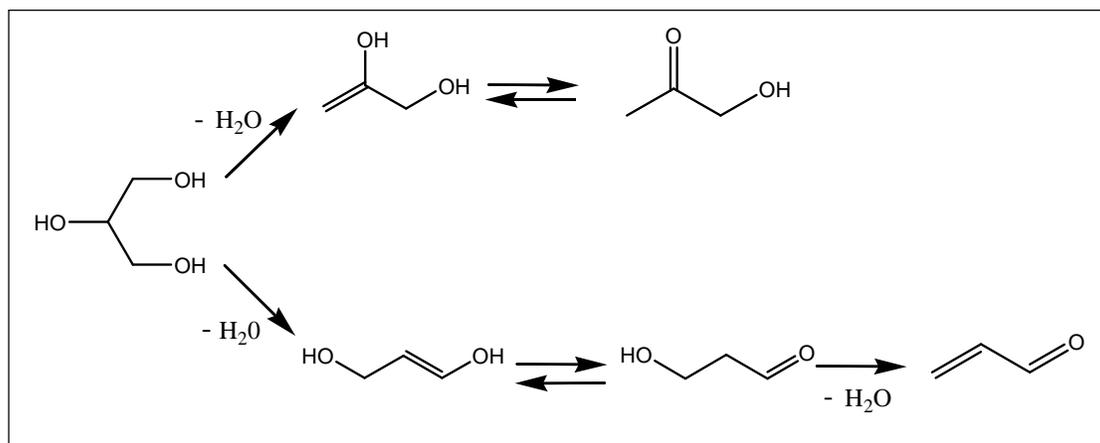


Fig.7. Reaction mechanism representing the formation of acrolein

#### ACKNOWLEDGMENT

One of the authors M. Prathap Kumar gratefully acknowledges DST, New Delhi for providing fellowship Under DST-INSPIRE programme.

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