CHAPTER – 2

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Synthesis of K₅[PW₁₁Mn(OH₂)O₃₉]. nH₂O

Synthesis of K₅[PW₁₁Cu(OH₂)O₃₉]. nH₂O

Synthesis of K₆[SiW₁₁Co(OH₂)O₃₉]. nH₂O

Synthesis of K₆[SiW₁₁Mn(OH₂)O₃₉]. nH₂O

Synthesis of K₆[SiW₁₁Cu(OH₂)O₃₉]. nH₂O

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Synthesis of H₅[PMo₁₀V₂O₄₀]. nH₂O

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2.1 Synthesis of heteropolycompounds

**Synthesis of K₅[PW₁₁TiO₄₀].nH₂O**

Solution of lithium acetate dihydrate (10 gm, 98.01 mmol) made in 30 ml water was brought to pH 6 with acetic acid. A solution of phosphotungstic acid (10 gm, 3.25 mmol) in water (35 ml) was added to form PW₁₁O₃₉⁻ in situ. Then one ml quantity of TiCl₄ was added dropwise with stirring. After the addition, the mixture was refluxed for 20 minutes, cooled to room temperature and filtered through an analytical filter aid. The precipitated solid was recrystallised from water.

**Synthesis of K₇[PW₁₀Ti₂O₄₀].nH₂O**

Sodium dihydrogen phosphate dihydrate (3 gm, 19.23 mmol) was added to a solution of solution of sodium tungstate dihydrate (15 gm, 45.47 mmol) in 50 ml water. Titanium tetrachloride (0.9 ml) was added dropwise with stirring. The mixture was refluxed for a period of 20 minutes followed by filtration through an analytical filter aid. The clear, colourless filtrate whose pH was 8.2 was cooled. To this was added solid potassium chloride (7.5 gm). The white product obtained was separated by filtration and recrystallized from water and used for catalytic study.

**Synthesis of K₂[Bu₄N]₅[PW₁₀Ti₂O₄₀].nH₂O**

Excess solid tetrabutyl ammonium bromide is added to the aqueous solution of K₇[PW₁₀Ti₂O₄₀]. The white coloured product obtained was recrystallized from water.

**Synthesis of Na₂₂₅[(CH₃)₂(C₆H₅)(C₆H₅CH₂)N]₄.₇₅[PW₁₀Ti₂O₄₀].nH₂O**

Sodium dihydrogen phosphate dihydrate (6 gm, 43 mmol) was added to a solution of sodium tungstate dihydrate (30 gm, 91 mmol) in 100 ml water. To this was added 1.8 ml of titanium
tetrachloride dropwise with constant stirring. The mixture was refluxed for a period of 20 minutes followed by filtration. The pH of the clear and colourless filtrate was checked to be 8.2. Then solid dimethyl phenyl benzyl ammonium chloride (4 gm) was added to obtain a blue precipitate which was separated by filtration and dried.

**Synthesis of K$_7$[PW$_{10}$Ti$_2$O$_{46}$] supported on silica (10 % w/w)**

The catalyst K$_7$[PW$_{10}$Ti$_2$O$_{46}$] (0.5 gm) was dissolved in 5 ml water. Coarse silica gel (4.5 gm) was added with constant stirring. The supported catalyst was obtained by evaporating the resultant slurry on a water bath, followed by drying overnight in an oven maintained at 110°C. The dried catalyst was then activated in a furnace at 300°C for four hours.

**Synthesis of K$_5$[PW$_{11}$Co(H$_2$O)$_{39}$].n H$_2$O**

Commercially available 12-phosphotungstic acid (11.2 g) was dissolved in 25 ml water containing 3 ml glacial acetic acid. The pH of the solution was adjusted between 5 and 5.5 with potassium bicarbonate. The solution was boiled and cobalt acetate tetrahydrate (0.8 g) in minimum quantity of water was added with stirring, followed by the addition of potassium acetate (15 g in 8 ml water and 0.5 ml glacial acetic acid). The hot solution was filtered and kept in refrigerator overnight. The purple solid that separated was filtered and air dried.

**Synthesis of K$_5$[PW$_{11}$Mn(H$_2$O)$_{39}$].n H$_2$O**

Hydrated 12-phosphotungstic acid (11.2 g) was dissolved in 25 ml water containing 3 ml glacial acetic acid. The pH of the solution was adjusted between 5 and 5.5 with potassium bicarbonate. The solution was boiled and manganese acetate tetrahydrate (0.8 g) in minimum quantity of water was added with stirring, followed by the addition of potassium acetate (15 g in 8 ml water and 0.5 ml glacial acetic acid). The hot solution was filtered and kept in refrigerator overnight. Yellow solid that separated was filtered and air dried.
Synthesis of $K_5 [PW_{11}Cu(H_2O)_{39}] \cdot n H_2O$

Hydrated 12-phosphotungstic acid (11.2 g) was dissolved in 25 ml water containing 3 ml glacial acetic acid. The pH of the solution was adjusted between 5 and 5.5 with potassium bicarbonate. The solution was boiled and copper acetate tetrahydrate (0.8 g) in minimum quantity of water was added with stirring, followed by the addition of potassium acetate (15 g in 8 ml water and 0.5 ml glacial acetic acid). The hot solution was filtered and kept in refrigerator overnight. Green crystals that separated were filtered and air dried.

Synthesis of $K_6 [SiW_{11}Co(H_2O)_{39}] \cdot n H_2O$

Hydrated 12-silicotungstic acid (11.5 g) was dissolved in 25 ml water containing 3 ml glacial acetic acid. The pH of the solution was adjusted to 6 with potassium bicarbonate. The solution was boiled and cobalt acetate tetrahydrate (0.8 g) in minimum quantity of water was added with stirring, followed by the addition of potassium acetate (15 g in 8 ml water and 0.5 ml glacial acetic acid). The hot solution was filtered and kept in refrigerator overnight. Deep red crystals that separated were filtered and air dried.

Synthesis of $K_6 [SiW_{11}Mn(H_2O)_{39}] \cdot n H_2O$

Commercially available hydrated 12-silicotungstic acid (11.5 gm) was dissolved in 25 ml water containing 3 ml glacial acetic acid. The pH of the solution was adjusted to 6 with potassium acetate. The resulting solution was boiled and then manganese acetate tetrahydrate (0.8 gm, 3.21 mmol) dissolved in minimum quantity of water was added slowly with stirring. This was then followed by the addition of a solution of potassium acetate (15 gm dissolved in 8 ml water containing 0.5 ml acetic acid). The hot solution was then filtered and kept in refrigerator overnight at 4°C. The yellow solid that formed was separated by filtration and then air dried.
Synthesis of K₆[SiW₁₁Cu(H₂O)O₃₉].ₙH₂O

Pure and hydrated 12-silicotungstic acid (11.5g) was dissolved in 25 ml water containing 3 ml glacial acetic acid. The pH of the solution was adjusted to 6 with potassium bicarbonate. The solution was boiled and copper acetate tetrahydrate (0.8 g) in minimum quantity of water was added with stirring, followed by the addition of potassium acetate (15 g in 8 ml water and 0.5 ml glacial acetic acid). The hot solution was filtered and kept in refrigerator overnight. The whitish blue solid that separated was filtered and air dried.

Synthesis of H₄[PM₀₁₁VO₄₀].ₙH₂O

Sodium phosphate dibasic dodecahydrate (1.77 gm, 5 mmol), was dissolved in 25 ml water and mixed with sodium metavanadate (1.52 gm, 12.5 mmol) made soluble in 25 ml boiling water. The mixture was cooled and acidified to red colour with 1.25 ml concentrated sulphuric acid. To this coloured solution was added sodium molybdate dihydrate (33.25 gm, 137.42 mmol) in 50 ml of water. Finally 21.25 ml of concentrated sulphuric acid was added. Colour of the solution turned to light red. After cooling the solution was extracted with four fractions each of 25 ml diethyl ether to isolate the heteropolyacid in a separating funnel. In this extraction the heteropoly etherate was present as the middle layer. After separation, a stream of air was passed through the heteropoly etherate layer to free it of ether. The orange solid that separated was dissolved in water, concentrated to the first appearance of crystal in a vacuum desiccator over concentrated sulphuric acid and then allowed to crystallize further. The orange crystals that formed were dried, crushed and used for further studies.

Synthesis of H₅[PM₀₁₀V₂O₄₀].ₙH₂O

Sodium metavanadate (4.06gm, 33.29 mmol) was dissolved by boiling in 16.6 ml water and then mixed with a solution of sodium phosphate dibasic dodecahydrate (1.18 gm, 3.29 mmol)
in 16.6 ml water. To the cooled solution was added 0.83 ml of concentrated sulphuric acid. The resulting solution developed a red colour. Addition of sodium molybdate dihydrate (20.16 gm, 83.32 mmol) in 50 ml water was then done. While the solution was stirred vigorously 14.16 ml of concentrated sulphuric acid was added slowly and then the hot solution was cooled to room temperature. The title compound was then extracted with four fractions each of 20 ml diethyl ether in a separating funnel. The heteropolyacid was present as the etherate in the bottom layer. This layer was isolated and dried in order to make it ether free. Orange coloured solid was obtained after complete drying. Pure complex was obtained after recrystallization in water. The crystals that formed were dried and crushed for further use.

**Synthesis of H₆[PMO₉V₃O₄₀]. nH₂O**

Sodium phosphate dibasic dodecahydrate (1.77 gm, 4.95 gm) was dissolved in 12 ml water. Sodium metavanadate (9.15 gm, 75.04 mmol) was made soluble by boiling in 50 ml water. The sodium phosphate solution was mixed with the sodium metavanadate solution. The resulting solution was cooled followed by the addition of 1.25 ml of concentrated sulphuric acid. This red coloured solution was then added to a solution of sodium molybdate dihydrate (13.62 gm, 56.3 mmol) in 37.5 ml water. This solution was stirred vigorously and simultaneously 21.25 ml of concentrated sulphuric acid was added. The hot solution was cooled to ambient conditions. The heteropolyacid formed was extracted with four fractions, each of 25 ml diethyl ether in a separating funnel. The heteropolyacid is present as the etherate in the middle fraction. The middle layer was then isolated, dried to free of ether. The resulting red coloured solid obtained was dissolved in water, concentrated to first crystal
formation and allowed to crystallize further. The red crystals that formed were dried and powdered prior to further use.

**Synthesis of [Bu₄N]₄[PMo₄V₀₄]ₙH₂O**

Commercially available 12- molybdophosphoric acid (5.9 gm, 2.86 mmol) was made soluble in 25 ml water. Solid lithium carbonate was added in small portions till the pH of the above solution reached 4.3. To this was added sodium metavanadate (0.32 gm, 2.66 mmol) dissolved in 25 ml hot water. The solution was cooled and the pH adjusted to 0.5 with 6M HCl. This solution was stirred in a round bottom flask on a magnetic stirrer for 48 hours at room temperature after which solid tetrabutyl ammonium bromide (4.83 gm, 30 mmol) was added. The immediately produced yellow powder was then stirred with additional 50 ml water for five hours, filtered off, washed thoroughly with 250 ml water, then twice with 50 ml ethanol and finally with 100 ml of diethyl ether (in two fractions of 50 ml). The yellow coloured powder obtained was dried in vacuo prior to further use.

**Synthesis of [NH₄]₄[PMo₁₁VO₄₆]ₙH₂O**

Solid ammonium chloride was added in excess to aqueous solution of H₄[PMo₁₁VO₄₆] to obtain a yellow coloured precipitate which was filtered and dried prior to use.

**2.2 Procedure: Catalytic reactions**

**2.2.1 Catalytic runs**

**Autoclave reactions**

The liquid phase oxidation reactions of substrates such as styrene, cyclohexene and para xylene were carried out under pressure in a stainless steel 300 ml capacity Parr autoclave.

Styrene oxidation was carried out by adding styrene (5.2 gm, 5 mmol), isobutyraldehyde (14.42 mmol), acetonitrile (solvent, 15 ml) and catalyst (65 μmol) to the autoclave. The
contents were pressurized with dry air to 440 psi. The temperature in the autoclave was maintained at 60°C under stirring for five hours. The products were analysed by gas chromatograph. Cyclohexene (4.1 gm, 5 mmol) was oxidised under similar conditions as styrene. The liquid products of cyclohexene oxidation were analysed by gas chromatograph and gas chromatograph mass spectrometer.

The liquid phase oxidation of p-xylene was carried out in a stainless steel 300 ml capacity Parr autoclave. The reactants, p-xylene (15 g, 140 mmol), water (15 g) tert-butyl hydroperoxide as the initiator (0.3 g) and the catalyst (0.096 mmol) were taken in the autoclave. The reactor was pressurised with air upto 400 psi and kept at 180 with stirring (600 rpm). After an induction period of 2 h, a sudden drop in pressure was observed suggesting the commencement of the oxidation reaction; heating and stirring were maintained till there was no further pressure drop. The autoclave was then cooled to 0° and gaseous products were released through a gas holder, collected and analysed. The reactor was further repressurised with air upto 400 psi and the reaction was continued at 180°. This operation was repeated once more. The solid product (6.5 g) was separated by filtration. A sample of the solid product was analysed by esterification by the following procedure: the solid product (0.1g) was dissolved in methanol (5 ml) and BF₃.MeOH (14% solution, 2 ml) was added and the mixture was then refluxed for 6 h. After cooling the sample, water was added and the esters formed were extracted with dichloromethane and analysed by GC. The filtrate portion of the oxidation product consisted of two layers: one was the aqueous layer while the second was organic. Both the layers were separated and analysed. The aqueous layer was extracted with dichloromethane before the GC analysis.
Reactions under atmospheric pressure

The liquid phase oxidation reaction of substrates like benzene, cyclohexane, methyl cyclohexane, naphthalene, methyl naphthalene, biphenyl and phenol were carried out under atmospheric pressure.

The hydroxylation of benzene was carried out in a two-necked 50 ml round bottom flask fitted with a water condenser and a glass stopper and placed in an oil bath maintained at 65°C. In a typical experiment, benzene (1.56 g, 20 mmol), aqueous hydrogen peroxide (2.36 gm, 20 mmol), catalyst (0.05 gm, 0.025 mmol) were mixed in 6 mL of acetonitrile and placed in the flask and contents were stirred with a magnetic stirrer. The reaction mixtures withdrawn at regular interval of 30 minutes were analysed by gas chromatography (Hewlett Packard gas chromatograph model No. 5890 Series-II) using HP-5 fused column with 30m x 0.53m x 1.0 μm film thickness and FID detector. Phenol formed in the reaction was confirmed by comparing the retention time with authentic standard and also by GCMS. From the moles of benzene reacted, turnover numbers were calculated. The samples were also analysed simultaneously by UV-Visible and EPR spectroscopy to identify the active intermediate species.

In case of cyclohexane oxidation the reaction was carried out in a two necked 50 ml capacity round bottom flask fitted with a water condenser and a glass stopper and immersed in an oil bath whose temperature was kept constant at 65°C. Thus the reaction mixture contained cyclohexane (1.68 gm, 20 mmol), aqueous hydrogen peroxide (2.36 gm, 20 mmol), catalyst (0.05 gm, 0.025 mmol) and 20 ml acetonitrile. The oil bath was kept on a magnetic stirrer to stir the reaction mixture. The reaction products were analysed by gas chromatograph. The
reaction mixture was subjected to $^{51}$V and $^{13}$C NMR spectroscopy at regular time intervals of half an hour.

In separate experiments methyl cyclohexane (1.96 gm, 10 mmol), naphthalene (1.28 gm, 10 mmol), methyl naphthalene (1.42 gm, 10 mmol), biphenyl (1.54 gm, 10 mmol) were dissolved in 20 gm, 5 gm, 8 gm and 5 gm of acetonitrile respectively, mixed with aqueous hydrogen peroxide (1.18 gm, 10 mmol) and catalyst (0.025 gm, 0.0125 mmol). The oxidation reactions were carried out under the same reaction conditions as that of cyclohexane and all the reactions were carried out for a period of one hour.

Phenol hydroxylation was carried out under atmospheric pressure. Thus phenol (1.88 gm, 20 mmol), $\text{H}_2\text{O}_2$ (2.36 gm, 20 mmol) are mixed together in 2.1 gm acetonitrile and catalyst (0.025 gm, 0.0125 mmol). The reaction was carried out at 65° C. Reaction parameters were varied to study the trends.

2.3 Procedures: Catalyst characterisation

2.3.1 Chemical analysis

The CHN analysis was done to determine the percentage of carbon, hydrogen and nitrogen present in the organic counter cation. The elemental analysis was done on Carlo Erba instrument (model no. EA 1108 elemental analyzer).

The other technique for chemical analysis included X-ray fluorescence carried out on a sequential wavelength dispersive X-ray spectrometer (Rigaku, 3070 E).

Atomic absorption spectroscopy was done on an atomic absorption spectrometer Hitachi model Z-8000. Standard solutions were used for calibration. Metals like V, Co, Mn and Cu were quantitatively estimated by this method.
2.3.2 Thermal analysis

This technique was used for determining the total number of water molecules present in heteropolycompound. The loss of weight corresponds to the loss of two different types of water molecules in the heteropolycompound. The thermal analysis was done on Seiko model instrument (TG/DTA 32). The rate of heating was kept at 10° C/minutes from 30°C upto 600°C under nitrogen atmosphere.

2.3.3 Infrared spectroscopy

The vibrational spectra of the samples were carried out to confirm the formation of the Keggin structure. The frequencies were indicative of the nature of the metal-oxygen bonds predominantly present in these type of complexes.

The FTIR spectra of the catalysts were recorded as nujol mulls at ambient temperatures between the range 4000 – 400 cm⁻¹. The spectra were recorded on a Shimadzu FTIR 8201 PC instrument.

2.3.4 UV-Visible spectroscopy

The electronic absorption spectra were recorded for structural and quantitative analysis. This kind of spectroscopy gives information about the electronic state of the compound.

The instrument in use was a Shimadzu UV-2101 PC UV – VIS spectrophotometer. The spectra were recorded at room temperature between the range 200 – 900 nm. The solution spectra were taken with reference to the respective solvent as the background. UV-Visible spectroscopy was useful for in situ characterisation of the reaction mixture for the determination and identification of the active intermediate species.
2.3.5 Electron paramagnetic resonance spectroscopy

This technique was used for determining the electronic state of the metal present in the heteropoly compound.

The solid and solution spectra were recorded at ambient temperatures on a Bruker EMX-X band spectrometer with 100 kHz modulation. The spin Hamiltonian parameters were determined by simulating the spectra using a Bruker Simfonia software package.

2.3.6 NMR spectroscopy

Structural elucidation of heteropoly complexes was achieved by this technique. It is a valuable tool to study the electron density distribution due to chemical shifts induced in the heteropoly compounds. Solid and solution NMR with $^{51}$V, $^{13}$C, nuclei was carried out on a Bruker instrument MSL 300. The measurements were carried out at 75.47 MHz for $^{13}$C and 78.9 MHz for $^{51}$V using a standard 10 mm probe. An external D$_2$O lock was used for all the measurements. The chemical shifts for $^{51}$V used VOCI$_3$ as the external standard while for $^{13}$C the standard was dioxane in D$_2$O.

2.3.7 Cyclic Voltammetry

This electrochemical technique is used for the study of redox active materials in heteropoly compounds. The transition metal substituted heteropoly compounds are studied for their redox behaviour by this method. Cyclic voltammetry is a tool to understand the rapid electron transfer between the metal ions. The feasibility of a particular reaction is dependent on the redox potential of the catalyst and the substrate. This can be easily determined using this technique. The cyclic voltammetry studies were carried out on an EG & G scanning potentiostat model attached with plotter model RE 0151.