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Research Article

Synthesis and Characterization of Tin(IV) Tungstate Nanoparticles – A Solid Acid Catalyst

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Abstract

Tin (IV) tungstate, a tetravalent metal acid salt was synthesized in the nanoform by chemical coprecipitation method using EDTA as capping agent. The material was found to be stable in mineral acids, bases and organic solvents except in HF and aquaregia. The material was characterized using EDS, TG / DTA, FTIR, XRD, SEM, HRTEM and BET surface area measurement. The molecular formula of the compound is $2SnO_2.3WO_3.5H_2O$ determined from elemental analysis using TG/DTA. Surface morphology and particle size were obtained using SEM and HRTEM. The surface area was found to be 205-225 m^2/g. The Na^+ exchange capacity found to be 3.8 meq/g, indicates the presence of surface hydroxyl group and hence the presence of Bronsted acid sites. The catalytic activity of the material was tested by using esterification and oxidation as model reactions. For the esterification of different alcohols, the percentage yield was found to be high for n-alcohol compared to isomeric alcohols. Oxidation of benzyl alcohol gives benzaldehyde and benzoic acid as the only products. © 2012 BCREC UNDIP. All rights reserved

Keywords: Tetravalent Metal Acid salt, HRTEM, Esterification, Oxidation, Catalyst

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1. Introduction

Nanometer-sized materials are attracting great interest in recent years due to the promising technological applications because of very different properties at the nanoscale as compared to those at the macrolevel. The physical laws applicable to the materials change as the size of the particles decreases to the nanoregime. Surface and quantum effects result in the modification of the properties [1].

Inorganic ion-exchangers are in general superior to organic exchangers because of their excellent stability towards temperature and radiation doses, hence can be used at elevated temperatures without being there any danger of decomposition. These synthetic ion exchangers are used in treatment of waste water, nuclear reactor for cooling water at high temperature and pressure, development of ion selective electrodes, construction of ion exchange membranes and their application to electrodialysis etc [2,3]. Among synthetic inorganic ion exchangers, acidic salts of multivalent metals deserve special mention because of their unique ion exchange properties along with several interesting applications.

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Tetravalent Metal Acid (TMA) salts have the general formula $M^{IV}(HXO_4)_2.xH_2O$ where M = Ti, Zr, Sn, Ce etc and X may be As, Mo, W, Sb etc. These materials provide exchangeable hydrogen ions when immersed in aqueous solution thus exhibiting cation exchange properties. The presence of replacable H^+ ions of the –OH groups make them to function as Bronsted acid catalysts. These materials were well studied in the amorphous form [4,5,6,7]. The synthesis of these materials in the nanoform will greatly influence the above mentioned properties as whole. The solution phase methods have been considered as one of the most promising routes for the synthesis of nanoparticles with advantages including less-complicated technique, low cost and large scale production [8].

In the present study, an inorganic ion exchanger, tin(IV) tungstate (SW) was synthesized in the nanoform by chemical coprecipitation method. The synthesized material has been well characterized using TG/DTA, FTIR, SEM, HRTEM, BET etc. The catalytic activity of the material was studied using esterification and oxidation of benzyl alcohol as model reactions.

2. Materials and Methods

2.1. Synthesis of tin (IV) tungstate nanoparticles

The raw materials used for the synthesis of tin (IV) tungstate were tin (IV) chloride ($SnCl_4.5H_2O$), sodium tungstate ($Na_2WO_4.2H_2O$) and ethylene diamine tetra acetic acid disodium salt, $[CH_2N(CH_2COOH)CH_2COONa]_2.2H_2O$. All the reagents used were of Analar grade. For the preparation of tin (IV) tungstate, in a 250 mL conical flask 25mL 0.02M EDTA was taken and 25mL of 0.2M tin (IV) chloride solution was added from a burette with constant stirring using a magnetic stirrer in order to obtain a homogeneous metal solution. To this, 50 mL of 0.2 M sodium tungstate was added gradually, drop by drop. After the addition of sodium tungstate, the pH of the solution was adjusted to 1-2 by adding 0.1 M HCl. The resulting reaction mixture was then stirred for two hours. The obtained gel was separated, washed with distilled water and then converted to the hydrogen form by immersing in 1 M HCl.

The chemical stability of the material in various media acids (HCl, H_2SO_4, HNO_3, HF and Aquaregia), bases (NaOH and KOH) and organic solvents (ethanol, benzene, acetone and acetic acid) were studied by taking 100 mg of each of synthesized material in 50 mL of the particular media and allowing to stand for 24 h. The change in color, nature and weight were noted.

2.2. Determination of ion exchange capacity (i.e.c)

The ion exchange capacity of the material was determined by column method. The column was prepared in a burette, provided with glass wool at the bottom. It was filled half way with distilled water, preventing air traps and then 0.5g of the ion exchanger was accurately weighed and transferred through a dry funnel. The water inside the column was kept at a level of about 1 cm above the material. In order to determine the Na^+ exchange capacity, a 250 mL solution of sodium acetate was added into the column and elution was carried out at a flow rate of 0.5 mL/min. The eluant was collected in a 500 mL conical flask and then titrated against 0.1 N NaOH solution. The i.e.c of the exchanger in milliequivalent per gram (meq gm^{-1}) is given by the relation,

$$\text{i.e.c} = \frac{a\,v}{w} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

where **a** is the molarity of the NaOH solution, **v** is the volume of the NaOH required for titration and ***w*** is the weight of the exchanger. The i.e.c were also determined for other alkali metals like Li^+ and K^+ and alkaline earth metal ions like Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} by the same method.

2.3. Characterization Techniques

In the present study, JOEL Model JED-2300 takes the EDS Spectrum of the sample. The TGA of the sample was recorded on a Shimadzu Thermal Analyzer at a heating rate of 10 °C/min. The FTIR Spectrum of SW was taken in the region between 4000-400 cm^{-1}. . X-Ray diffractogram (2θ=10-90°) was obtained on XPERT-PRO powder diffractometer with Cu-Kα radiation. SEM of sample was taken from JEOL Model JSM-6390LV instrument. HRTEM of the sample was taken using 300 kV HRTEM (FEI – Model) Tecnai 30 G2 instrument. Surface area measurement (BET method) was carried out on Micromeritics Gemini at -196ºC using nitrogen adsorption isotherms.

2.4. Esterification

The esterification reaction was carried out in a round bottomed flask (100 cm^3) fitted with a water cooled condenser. The temperature was maintained at 110 °C using an oil bath connected to a thermostat. In a typical reaction, acetic acid and alcohol were taken in the ratio 2:1 directly into the round bottomed flask along with the catalyst. To this reaction mixture, 10-15 mL of a suitable solvent such as toluene or cyclohexane was added. Cyclohexane was used as the solvent for synthesis of ethyl acetate and toluene for other acetates. Reaction mixture was refluxed for 2.5 hours. Products were analysed using GC-MS (carbowax column). The reaction conditions were optimized after changing the reaction conditions like ratio of acid to alcohol, amount of catalyst and solvent.

2.5. Oxidation

Oxidation of benzyl alcohol (BA) was carried out in a 100mL round bottom flask equipped with water condenser. First, a mixture of benzyl alcohol and hydrogen peroxide was taken in 1:1 volume ratio and 1 mL acetonitrile (CN) was added as solvent. To this 100 mg catalyst was added and refluxed for two and half hours at two different temperatures i.e. 85 and 110 °C. The reactions were also carried out in the absence of acetonitrile and catalyst. The products were analyzed using GC-MS.

3. Results and Discussion

Tin (IV) tungstate was obtained as a lemon yellow powder. The material was found to be stable in mineral acids and bases at all concentrations as evidenced by no change in color, form or weight of the sample used except in HF and aquaregia. The exchanger was also stable in alkali and alkaline earth metal ions. The ion exchange capacities for alkali metal ions, Li^+, Na^+ and K^+ were found to be 2.6, 3.8, 4.2 meq/g while for alkaline earth metal ions Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} it was found to be 2.5, 2.8, 3.6 and 4 meq/g.

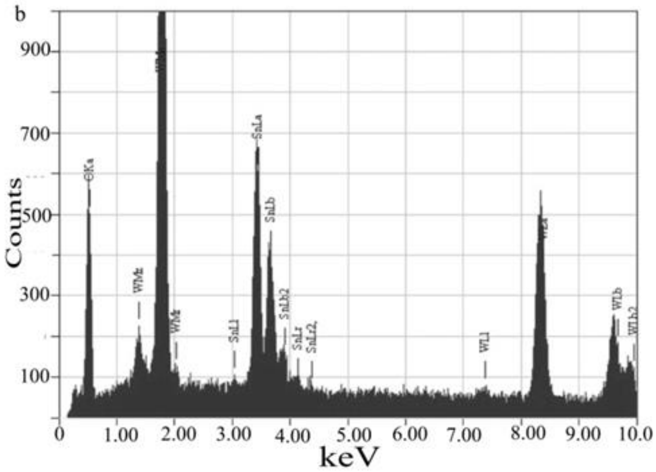


Figure 1: Energy Dispersive Spectrum of tin (IV) tungstate nanoparticles

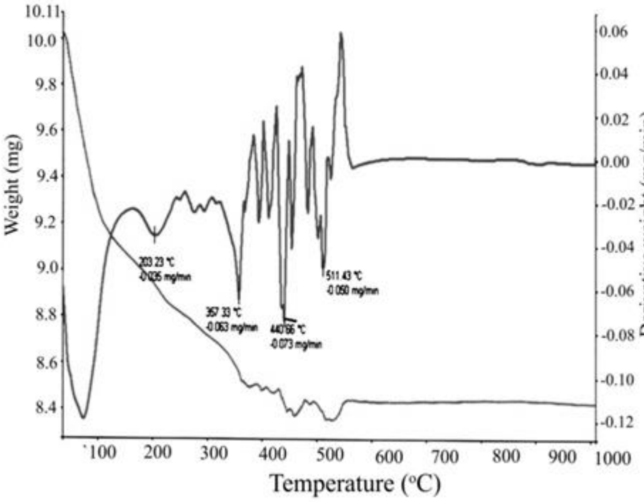


Figure 2: TG/DTA of tin (IV) tungstate nanoparticles

The EDS spectrum of SW is shown in Figure 1 and it shows 23.65% tin, 55.49% tungsten and 20.86% oxygen. The ratio of Sn to W is 2:3 and the empirical formula calculated on the basis of this percentage composition is $2SnO_2.3WO_3.nH_2O$. TG/DTA of SW is shown in Figure 2. It shows 8% weight loss up to 100 °C due to the loss of external water molecules. The corresponding DTA curve shows an endothermic peak ~70 °C. After 100 °C, a gradual weight loss is observed, which may be due to the condensation of structural hydroxyl groups. In the temperature range between 350 and 550 °C, several endothermic and exothermic peaks are observed due to the phase change occurring in the compound. Above 550 °C, no weight loss is observed because the compound is converted to its oxide. The 8% weight loss of mass occurred for SW represented by TGA curve at 100 °C must be due to the loss of external water molecules.

The value of '**n**' the number of external water molecules was calculated using the relation,

$$18\,n = \frac{X(M + 18n)}{100} \;..............\; (2)$$

where X is the percentage weight loss in the exchanger by heating up to 100 °C, and **(M+18n)** is the molecular weight of the material [9]. This gives a value of 5 for the number of external water molecules per molecule of the exchanger. Based on TG data and elemental analysis, the formula assigned to the sample is,

$$SW - 2SnO_2\ 3WO_3.5H_2O..............(3)$$

FTIR spectrum of tin(IV) tungstate is shown in Figure 3. The sample exhibits intense and broad

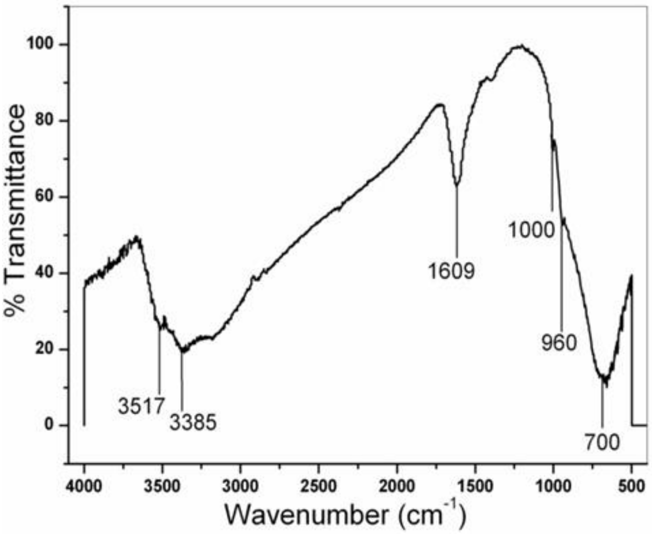


Figure 3: FTIR spectrum of tin(IV) tungstate nanoparticles

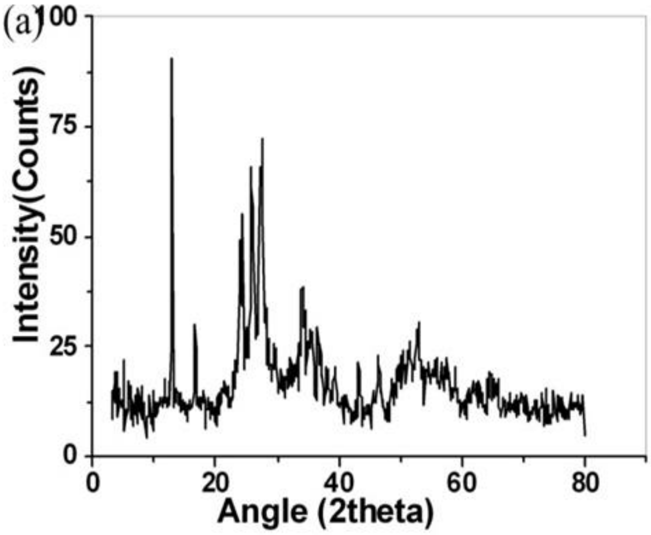


Figure 4: XRD spectrum of tin(IV) tungstate nanoparticles

resonance owing to –OH stretching modes ranging from ~3600 to ~2500 cm^{-1}. Below 2000 cm^{-1} the spectrum consists of a resonance at 1617 cm^{-1} due to water deformation. A band at 1000 cm^{-1} is due to W=O. Wide bands at 659 cm^{-1} and 561 cm^{-1} are assigned to Sn-O-Sn and Sn-O (belonging to Sn-OH groups) stretching vibrations respectively. The reported data with the band around 650 cm^{-1} corresponds to Sn-O frequency of SnO_6 octahedra. In this material this band is observed at 659 cm^{-1} [10,11].

X-ray diffractogram of SW is shown in Figure 4. The sharp peak represents the crystalline nature of the synthesized nanoparticles. The average diameter of nanoparticles were calculated from the line broadening of the XRD pattern, making use of Scherrer formula,

$$D = \frac{0.9\,\lambda}{\beta\ \mathrm{Cos}\ \theta} \ldots\ldots\ldots\ldots..(4)$$

where **D** is the crystallite size in nm, λ is the radiation wavelength (0.15406 nm for Cu Kα radiation), **β** is the full width at half maximum of the X-ray line (radians) and **θ** is the diffraction peak angle [12,13]. The particle size calculated was found to be 15.64nm. The diffraction data compared with standard JCPDS file show that it consists of orthorhombic SnO_2 (Card No. 78-1063) and W_3O_8 (Card No.81-2262).

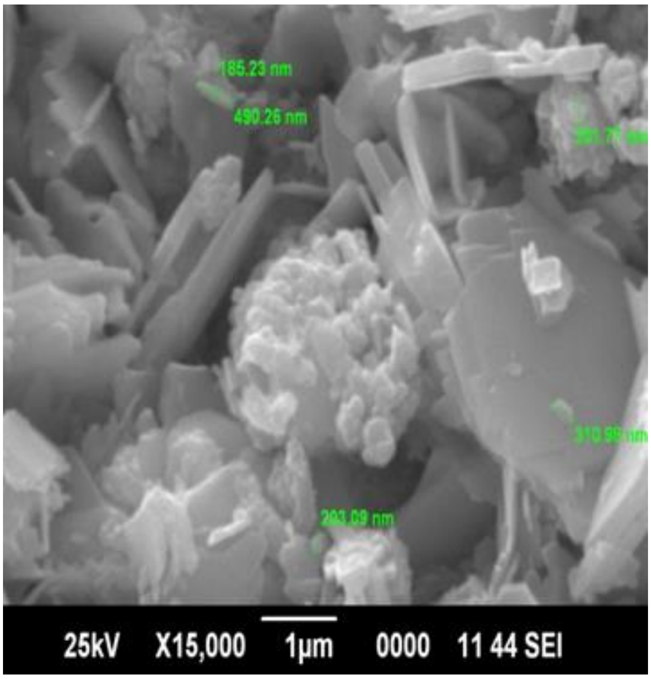


Figure 5: Scanning Electron Microscopy image of tin(IV) tungstate nanoparticles

The Scanning Electron Microscope (SEM) and High Reolution Transmission Electron Microscope (HRTEM) images of the synthesized material are shown in Figures 5 and 6 respectively. The SEM picture shows plate like appearance. The particle size obtained from HRTEM is 20 nm. It shows agglomeration of particles. The particle size calculated from XRD and that obtained from HRTEM are often different. This is because of peak broadening caused by inhomogeneous strains, twinned structure, lattice bending or other point defects. Hence Scherrer equation gives results different from actual size [14]. The surface area was found to be 205-225 m^2/g.

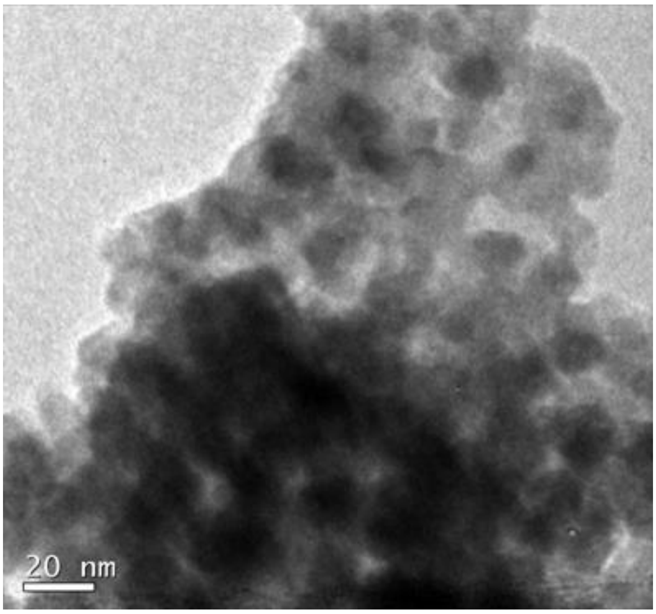


Figure 6: HRTEM image of tin (IV) tungstate nanoparticles

Esterification reaction is relatively slow and need activation either by high temperature or by a catalyst to achieve equilibrium conversion to a reasonable amount. Esterification is reversible and equilibrium constants for these reactions are low. One of the products during estereification is water. In order to obtain higher yield of esters, the reaction must be forced to completion by either removing the water produced or by operating with an excess of one of the two reactants, acid or alcohol. Following this principle, in the present work, acid was taken in excess. The presence of water provides negative effect on the acid-catalyzed reactions, since water interfaces with the catalysts and reduces catalyst performance. In addition, the presence of water during the esterification reaction could result in the occurring of hydrolysis reaction, which eventually reduces the production yield. The effect of co-solvent adding increases the production yield. Solvents cyclohexane and toluene were employed to remove the water formed during the reaction as a binary azeotrope, so that reverse reaction is avoided [15,16]. Table 1 shows the percentage yields of various esters formed by using the catalyst SW nanoparticles. In the case of isomeric alcohols, the yield decreases in the order $1^{\circ} > 2^{\circ} > 3^{\circ}$. The lower yield of tertiary alcohols may be due to the steric interaction [17]. In the case of regenerated sample, the yield decreases by 5%. The yield becomes constant on further regeneration. Among the monoesters, higher yield is obtained in the case of benzyl acetate which could be attributed to the enhanced nucleophilicity due to the presence of aromatic ring in benzyl alcohol. The possible mechanism of the reaction is given in Scheme 1.

Table 1: % yield of esterification of acetic acid with different alcohols

Case	Ester formed	% yield
1	Methyl acetate	78
2	Ethyl acetate	82
3	Propyl acetate	75
4	Isopropyl acetate	60
5	Butyl acetate	78
6	2^{o}-Butyl acetate	64
7	3^{o}-Butyl acetate	57
8	Amyl acetate	84
9	Benzyl acetate	85

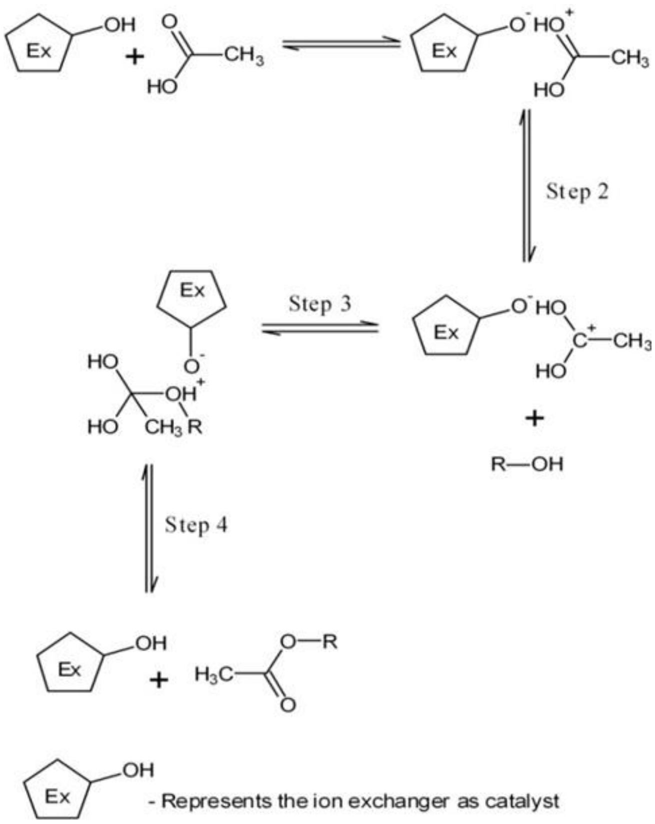
Oxidation of benzyl alcohol gives benzaldehyde, benzoic acid and benzyl benzoate as products. In the present study only benzaldehyde and benzoic acid were obtained as the products. The percentage yield was found to be high using a small quantity of the catalyst (100 mg). The reactions were carried out at two different temperatures with and without a solvent. This reaction was slowly preceded in the absence of the catalyst. A similar observation was also noted by other authors [18]. As shown in table 2, the percentage yield was found to be very low in the absence of the catalyst. However on using SW nanoparticles as catalysts the yield was found to be almost doubled. The selectivity was found to be high for benzoic acid on using this catalyst but without catalyst only benzaldehyde was obtained as major products.

The results obtained from the oxidation of benzyl alcohol along with experimental conditions

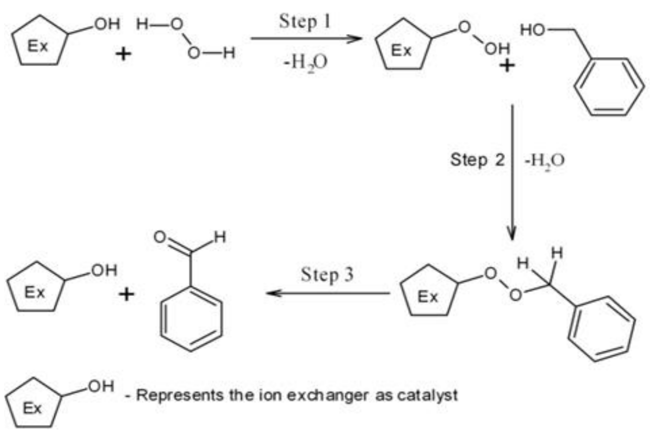
Table 2: Results of oxidation of benzyl alcohol, % conversion and % selectivity

Case	BA :H_2O_2 & temp. (°C)	CN (mL)	% yield	Selectivity(%)	
				-CHO	-COOH
1	1:1,110°C	1	74.00	12.08	87.91
2	1:1,110°C	-	72.18	14.78	85.21
3	1:1,82°C	1	62.60	09.82	90.17
4	1:1,82°C	-	60.61	15.09	84.91
5*	1:1,82°C	1	30.00	84.34	15.65
6*	1:1,82°C	-	25.00	77.70	22.29

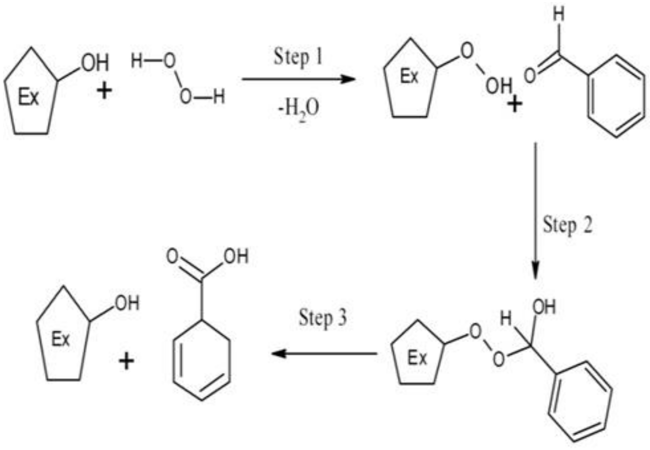
*Reactions were carried out in the absence of catalyst



Scheme 1: Possible mechanism of esterification



Scheme 2: Probable mechanism for the oxidation of benzyl alcohol into benzaldehyde



Scheme 3: Probable mechanism for the oxidation of benzaldehyde into benzoic acid

are summarized in the Table 2. The probable mechanism for the oxidation of benzyl alcohol is given in Schemes 2 and 3.

The formation of metal peroxo compound with hydrogen peroxide and subsequent transfer of the peroxidic oxygen to the organic reactant has been proposed as the mechanism [19]. The exchanger contains WO_x descrete clusters with tungsten in +6 oxidation state. Bronsted acid sites were formed from these clusters when a lower valent element such as Sn^{4+} replaces W^{6+} or when W^{6+} centers reduces slightly during catalytic reaction [20]. The catalyst contains W=O oxospecies on the discrete clusters which converts to W-OH species after the introduction of water or moisture. In this type of catalysts, Bronsted acid sites were also formed in-situ by partial reduction during catalytic reactions [21].

4. Conclusion

Nanoparticles of tin (IV) tungstate, an ion exchanger belonging to the class of TMA salts was synthesized by chemical coprecipitaion method and well characterized. The molecular formula found out using EDS with the help of TG/DTA is $2SnO_2.3WO_3.5H_2O$. The material is crystalline and particle size determined using XRD is 15.64 nm. Esterification of acetic acid with different alcohols was successfully carried out. Oxidation of benzyl alcohol was successfully carried out using this ion exchanger. Eventually, the present study reveals the promising use of this catalyst in various industrially important reactions.

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