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A chemical synthetic route for the preparation of fine-grained metal tungstate powders (M = Ca, Co, Ni, Cu, Zn)

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Abstract

Nanocrystalline metal tungstate [i.e. MWO_4 where M = Ca(II),Co(II),Cu(II), Ni(II), and Zn(II)] powders have been prepared from the complete evaporation of a polymer based metal-complex precursor solution. The metal ions are in aqueous solution through complexation with triethanolamine (TEA) and are dispersed in a polymeric reagent composed of an aqueous solution mixture of sucrose and polyvinyl alcohol (PVA). The mesoporous carbon rich precursor powders has been obtained on complete dehydration of the precursor solution and generates the respective metal tungstate phase after complete removal of carbonaceous residue at a heat treatment temperature less than 500°C. X-ray diffractometry (XRD), differential thermal and thermogravimetric analysis (TG/DTA), and transmission electron microscopy (TEM) have been used to characterize the precursors and the heat-treated final powders. The average particle sizes as measured from X-ray line broadening and transmission electron microscopy studies are around ~15–40 nm. The particles have sizes of the same order to that of crystallite indicate the poor agglomeration of crystallites. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: (M)WO_4; Powders — organic precursors; Tungstates; X-ray methods

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1. Introduction

Fine grained (i.e. particle diameters less than 100 nm) mixed oxides ceramic materials due to their crucial microstructure based properties, brought about by dimensional manipulations, have potential application in many areas of technology.[1,2] Over the last few decades a lot of attentions have been focussed on the synthesis and processing of these nanosized mixed-oxide ceramic powders and it has been established that the method of preparation significantly influences the microstructure (i.e. particle size, texture etc.) of the final powders.[3]

The solution based chemical synthetic methods play a crucial role in the design and production of fine ceramics and have been successful in overcoming many of the limitations of the conventional solid state method. The use of chemistry can avoid three major problems — long diffusion paths, impurities and agglomeration. The reasons are being that the chemically prepared powders require shorter diffusion distance due to improved homogeneity.

Several solution based chemical synthesis methods have gained popularity for the preparation of the fine ceramic oxide powders. They include the sol-gel,[4–6] co-precipitation,[7] hydrothermal,[8,9] citrate gel and other-gel[10–14] combustion[15,16] methods etc. In this paper, we report the preparation of several nanosized metal tungstate powders [such as: $CaWO_4$, $CuWO_4$, $CoWO_4$, $NiWO_4$, $ZnWO_4$] from complete dehydration of a solution comprising the metal ion—complexed with—triethanolamine, polyvinyl alcohol and sucrose. Evaporation is accompanied by the decomposition of the metal complexes. The decomposition results in a voluminous, organic based, black, fluffy mass of carbonaceous material which on complete removal through aerial oxidation produces fine powders of metal tungstates having the general molecular formula MWO_4 (where M = Ca,Co, Ni,Cu,Zn). Calcium tungstates, of the scheelite structural family, for example are of commercial interest for applications in lasers, and fluorescent lamps because of their attractive photoluminescence properties[17–19] while some of the transition metal tungstates (TMT) are of especial importance because of their electrical conductivity,[20,21]

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and magnetic properties.[22] These materials also find application as catalysts[23] and humidity sensors.[24]

This communication is aimed to prepare nanosized tungstates of bivalent metals to use as catalyst for oxidation of olefinic compounds with hydrogen peroxide producing diols in liquid phase.

2. Experimental

2.1. Raw materials used for this are

(a) Sodium tungstate (99%) BDH Chemicals, India. (b) Metal nitrate salts [M = Ca(II), Co(II), Cu(II), Ni(II), Zn(II)], (99.9%) E Merck India Ltd. (c) Triethanolamine E Merck India Ltd. (d) Sucrose, E Merck India Ltd. (e) Polyvinyl alcohol (i.e., PVA) SD's Fine Chemical, India.

2.2. Preparation of precursor powders

The desired metal nitrates [i.e. $Ca(NO_3)_2/Cu(NO_3)_2/Co(NO_3)_2/Ni(NO_3)_2/Zn(NO3)_2$] were individually dissolved in deionised water. Ten milliliters of 0.01 M metal nitrate solution was poured into an equal volume of an aqueous solution of sodium tungstate (0.01 M) maintaining stoichiometric ratio 1:1. It precipitated out the respective metal tungstates from the solution. The metal tungstates were collected on filtration and were thoroughly washed with water to make them free of sodium ions. These precipitated tungstates of the various metal ions after simple drying did not produce nanosized powder due to strong chemical agglomeration. These precipitated tungstates of various metal ions were analyzed using an atomic absorption spectrophotometer to check for the metal ions and tungstate ion stoichiometries, which were found to be 1:1.

The metal tungstate precipitate (10 mM) was then qualitatively transferred to a beaker containing 100 ml of distilled water. Triethanolamine (40 mM) (4 mol per unit mol of metal cation) was added to the solution and heated in a water bath at around 60°C to get a clear homogeneous solution. The pH of the solution was between 11 and 12. A 40 mM aqueous solution of sucrose (4 mol per unit mol of metal cation) and 1 mM PVA (10 mol of monomer w.r.t the total mol of the cation) dissolved in 5ml of water were added to the previous solution under hot conditions to produce the homogeneous precursor solution. After addition of sucrose and PVA the pH of the solution did not change. The details of the reagents required and their respective molar compositions are represented in Table 1.

Table 1
Mol ratios of various reagents required for the preparation of the various metal tungstate precursors

System	Metal ions (moles)	Sodium tungstate (mol)	Triethanolamine	Sucrose (mol)	PVA[a] (mol)
$CuWO_4$	0.01	0.01	0.04	0.04	0.001
$NiWO_4$	0.01	0.01	0.04	0.04	0.001
$CoWO_4$	0.01	0.01	0.04	0.04	0.001
$CaWO_4$	0.01	0.01	0.04	0.04	0.001
$ZnWO_4$	0.01	0.01	0.04	0.04	0.001

[a] Mol of vinyl alcohol monomer unit of PVA.

The resultant homogeneous precursor solution was then put to heat (at ~200°C) with continuous stirring and was eventually evaporated to dryness. Near the end of the evaporation the precursor solution gave rise to a fluffy black organic mass. The effective surface area of this carbonaceous mass is about 500–630 m^2/g. The metal ions formed clusters with the tungstate ions and remained embedded in the resulting matrix of the mesoporous carbon. The carbon rich mass was easily crushed to constitute the precursor powders. The precursor powders were subsequently heat-treated at a temperature range between 300 and 600°C along with variations in the period of time. The various virgin precursor powders of the metal tungstates were characterized before and after heat-treatment.

The over all chemical reaction is

$$M^{2+} + Na_2WO_4 \rightarrow MWO_4 + 2Na^+$$

$$MWO_4 + N(CH_2CH_2OH)_3 \rightarrow [MN(CH_2CH_2OH)_3]^{2+}WO_4$$

$$[MN(CH_2CH_2OH)_3]^{2+}WO_4 \xrightarrow{\text{aerial oxidation}} MWO_4 \quad \text{(nano sized)}$$

3. Results and discussion

Simultaneously recorded thermogravimetry (TG) and differential thermal analysis (DTA) studies of the various precursor powders were carried out in air using thermal analyzer (model: DT-40. Shimadzu Co., Kyoto. Japan) at a heating rate of 10°C min^{-1}. The DTA curve for the all the samples, prepared in the presence of sucrose and PVA, showed an exothermic peak between the temperature range 300–550°C, which could be attributed to the catastrophic exothermic oxidation of the carbonaceous mass remaining from PVA, sucrose and TEA. The entire thermal effect was accompanied by the evolution of various gases (such as: CO, CO_2, water-vapor etc.) that was manifested by a single step weight loss in the TG curve. The DTA/TG curve for the $CaWO_4$ precursors is depicted in Fig. 1 as a typical representative.

The room temperature X-ray powder diffraction (XRD) studies of the various virgin precursor powders and their corresponding heat-treated forms were carried out using a Philips diffractometer (model: PW1710 and PW 1810, Philips Research Laboratories, Holland) with CuK_α radiation. The X-ray diffractograms of the $NiWO_4$, and $ZnWO_4$ precursor powders are depicted in Figs. 2 and 3 respectively. The X-ray diffraction studies of the precursors of the samples $CuWO_4$, $CoWO_4$ and $NiWO_4$ prepared in the presence of sucrose and PVA showed diffraction lines characteristic of the respective metal tungstate phase. This indicates that the crystallization of the tungstate phases occur in the virgin sample itself (i.e. during the complete evaporation of the precursor solution on the hot plate at temperatures ~200°C). The X-ray diffractograms of the virgin precursors of the samples $CaWO_4$ and $ZnWO_4$ was, however, marked by the absence of any prominent diffraction lines reflecting their X-ray amorphous nature. The respective tungstate phase eventually crystallized in these samples on heat-treatment of the virgin precursor powders. The respective heat-treatment temperatures required for the initiation of the crystalline phase and temperatures required to get the carbon free metal tungstate powders are given in Table 2.

After complete evaporation of the precursor solution the residual carbonaceous mass started burning slowly in presence of metal ions like Cu^{2+},Co^{2+},Ni^{2+} generating heat. The burning of residual carbon was spontaneous due to the catalytic effects of Cu^2, Co^{2+}, Ni^{2+}. The presence of Cu^{2+},Co^2,Ni^{2+} ions helped the faster burning generating higher local temperature which helped to produce crystallites of metal tungstates from the amorphous material formed initially.

However similar phenomena did not occur in case of Ca^{2+} or Zn^{2+} containing system. Due to comparatively lower catalytic activity of the Ca^{2+} and Zn^{2+} than that of Cu^{2+}, Co^2, Ni^{2+} the in situ temperature generated during oxidative decomposition of the carbonaceous material was not sufficient for the crystallization of the tungstate phase in the virgin precursor material hence they appeared amorphous to X-ray. For this reason higher calcination temperatures were required to get the desired metal tungstate phases of Ca^{2+} and Zn^{2+}.

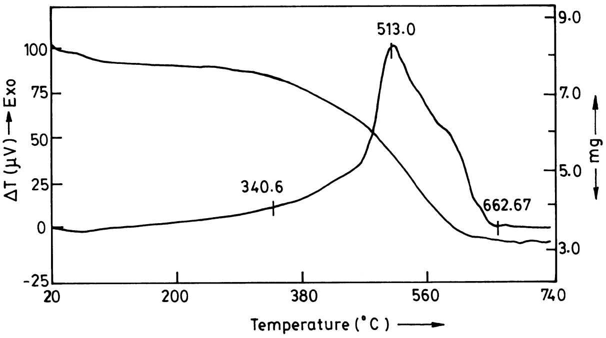

Fig. 1. Thermal Studies of the $CaWO_4$ precursor powders prepared in presence of sucrose and PVA.

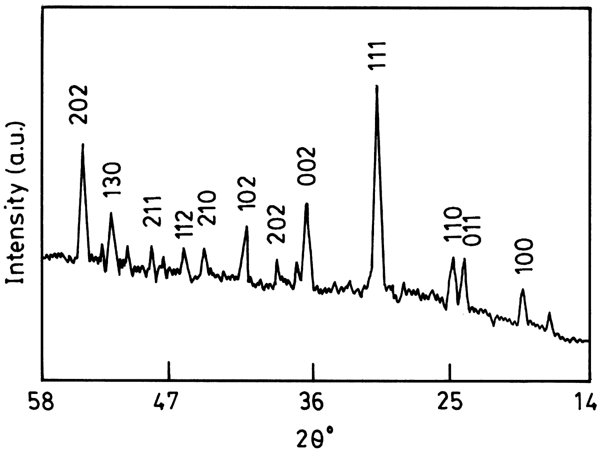

Fig. 2. The X-ray diffractograms (using CUK_α radiation) of the virgin $NiWO_4$ precursor powders prepared in presence of sucrose and PVA.

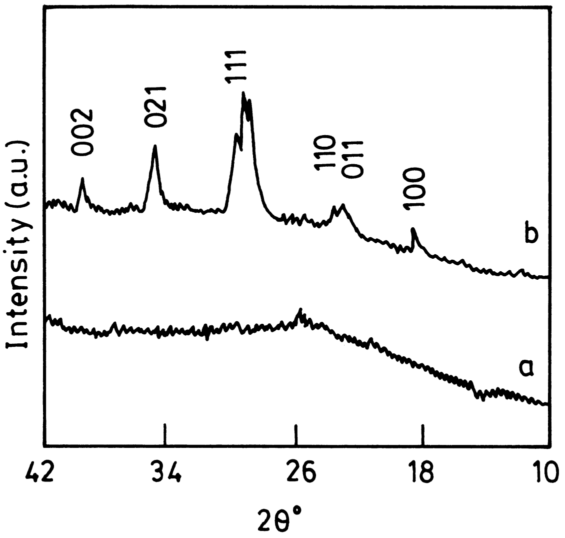

Fig. 3. The X-ray diffractograms (using CuK_α radiation) of the $ZnWO_4$ system prepared in presence of sucrose and PVA: (a) virgin precursor powder, and (b) after heat-treatment at 450°C/3 h.

Table 2

Summary of the state of the various virgin precursors and the metal tungstate phase formation temperatures

System	X-ray phase of Virgin precursor	Temperature[a] (°C)	Temperature[c] (°C)
$CuWO_4$	Crystalline	~200[b]	400/2h
$NIWO_4$	Crystalline	~200[b]	400/2h
$CoWO_4$	Crystalline	~200[b]	400/2h
$CaWO_4$	Amorphous	450/4h	500/2h
$ZnWO_4$	Amorphous	450/3h	500/2h

[a] The minimum heat-treatment temperatures required for the formation of the desired metal tungstates phase from the amorphous virgin precursors.

[b] Heat-treatment temperature of ~200°C signifies the hot plate temperature during complete evaporation of the precursor solution.

[c] The minimum heat-treatment temperature required for getting the carbon free metal tungstate powders.

The crystallite size for the crystalline precursors and the heat-treatment powders, were calculated from the X-ray line-broadening studies using the Scherrers' equation.[25] The details of the crystallite size for the various metal tungstate systems prepared with addition of sucrose and PVA in the precursor solution, are summarized in Table 3. Comparative studies had been made in presence and absence of PVA and sucrose. It reveals that the presence of PVA and sucrose mixture produces the finest particle with narrow size distribution. Either of PVA or sucrose did not produce similar characteristic of the powder. The concentration of PVA and sucrose were optimized of $CoWO_4$ for getting smallest particle size with minimum formation of carbonaceous mass and it was found to be metal ion: sucrose mole ratio 1:4 and metal ion: monomer PVA ratio 1:0.1. It is presented in Figs. 4 and 5.

The average particle diameters of the heat-treated tungstate powders were measured using a transmission electron microscope (TEM) (model: Philips TM300 Philips Research Laboratories, Holland). The bright field TEM micrographs reflected the basic powder morphology where the smallest visible isolated spot can be identified with the particle/crystallite agglomerate. The bright field TEM micrograph for the heat-treated (at 500°C/2 h) $CoWO_4$ precursor powders prepared in the presence sucrose and PVA is represented as typical examples in Fig. 6(a). From the TEM studies of the metal tungstate powders prepared in the presence of sucrose and PVA [Fig. 6(a)] it was observed that the particles were almost spherical with average particle diameters ranging between 15 and 40 nm. The corresponding selected area electron diffraction pattern of the samples [Fig. 6(b)] showed distinct rings, characteristic of an assembly of nanocrystallites.

Table 3
Summary of the particle sizes obtained from X-ray diffraction and TEM characterization studies

System	Cryst. size[a] (nm)	Particle size[b] (nm)
CuWO4	20	28
NiwO4	10	20
CoWO4	12	18
CaWO4	33	38
ZnWO4	25	32

[a] Average value of the crystallite sizes calculated using the Scherrers' formula applied to the various d_{hkl} lines of the precursor powders heat-treated at 500°C/2 h.

[b] Average of the smallest visible isolated particle/crystallite agglomerate as observed from TEM studies for the respective precursor powders heat-treated at 500°C/2 h.

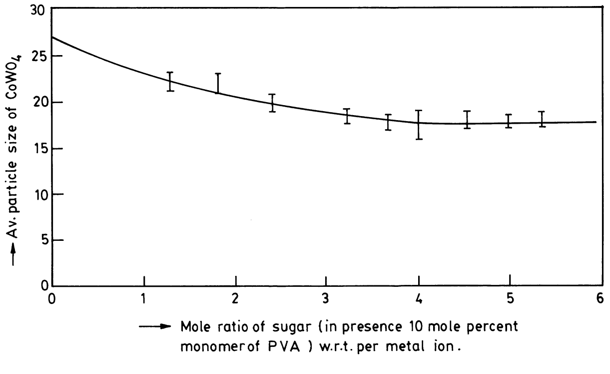

Fig. 4. Variation of particle size of $CoWO_4$ with the variation of sugar content.

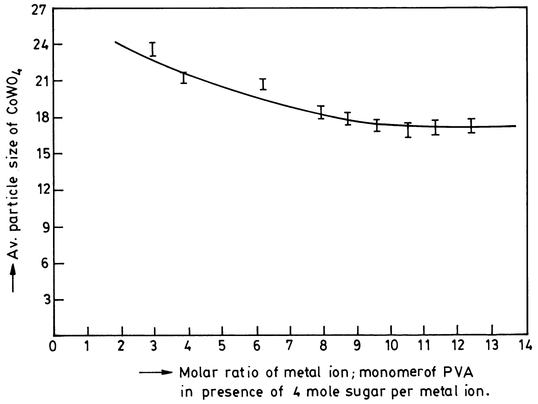

Fig. 5. Variation of particle size of $CoWO_4$ with the variation of PVA content.

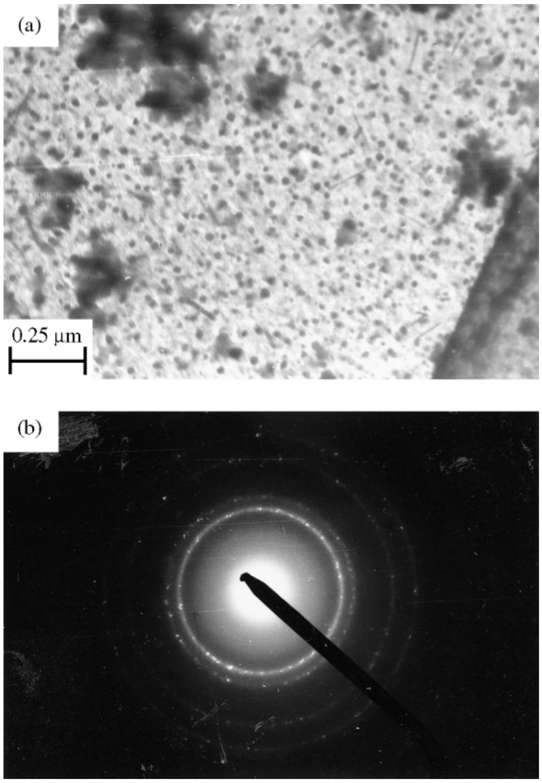

Fig. 6. (a). The bright field TEM micrograph of the $CoWO_4$ precursor powders, prepared in presence of sucrose and PVA, after heat-treatment at 500°C/2h. (b). The corresponding selected area electron diffraction pattern for the $CoWO_4$ powders, prepared in presence of sucrose and PVA, heat-treated at 500°C/2 h.

In this preparative method PVA and sucrose was added to form a highly porous carbonaceous material after complete evaporation of the precursor solution. Only PVA could fulfill the purpose but due to its graphite formation tendency, it was partially replaced by sucrose or any other polyhydroxy hydrocarbon. The sucrose or polyhydroxy hydrocarbon in presence of PVA formed mesoporous carbonaceous residue, which volatilized through low temperature aerial oxidation. The effective surface areas of these carbonaceous masses were very high. It ranged between 500 and 650 m^2/g. Only the polyhydroxy hydrocarbon/sucrose did not form these types of mesophases.

This is probably due to chemical bonding of sucrose with PVA, in which sucrose tags on to the PVA backbone, as the pendant group results in a highly branched polymeric structure. This type of structure is very suitable for generation of mesoporous carbon. PVA and sucrose mixture can act as a precursor for formation of a branch polymer, which easily transforms into mesoporous material. The removal of residual carbon becomes easy when transition metal having variable oxidation states is associated with it. Carbonaceous material due to the high catalytic activities of the transitional metal ions (Cu^{2+}, Co^{2+}, Ni^2) for aerial oxidation of the carbonaceous material. Before dispersion of the metal ions in the polymeric matrix, they were complexed with TEA where the TEA served as a chelating agent having efficient coordination properties with the metal ions avoiding any intermittent precipitation from homogeneous solution.

After complete dehydration of the precursor solutions which resulted in a mesoporous carbon-rich mass embedded with the clusters of metal ion-tungstate ion in the matrix. The carbonaceous precursor powders, after heat-treatment in air, at temperatures between 200 and 500°C, volatilized through the aerial oxidation carbon and it resulted in the formation of nanocrystals of the respective metal tungstates.

4. Conclusion

A simple chemical process has been developed for the preparation of various nanosized metal tungstate powders starting from a polymer based metal-complex precursor solution.

The principle was to keep the metal tungstate in solution through complexation, where metal ion forms a water-soluble complex cation with TEA and tungstate ion remains as a salt of organic base, which is TEA. It disperses the inorganic ions atomistically in a matrix produced by thermal decomposition of polymeric reagent composed of sucrose and PVA, through the formation of mesoporous carbonaceous mass embedded with nano particles of metal-tungstates. After complete volatilization of carbonaceous mass through aerial oxidation, it leaves nanosized metal-tungstate powder.

The developed method is technically simple, versatile and uses easily available laboratory reagents hence is suitable for low cost preparation of high quality nanocrystalline metal tungstates.

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