A novel chemical route for the preparation of nanosized oxides, phosphates, vanadates, molybdates and tungstates using polymer precursors

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Abstract. A variety of nanosized (particle diameter ranging between 10–90 nm) ceramic oxide powders have been prepared from a versatile, efficient and technically simple polymer matrix based precursor solution. The precursor solution constituted of the metal nitrates mixed with the polymer-PVA/PAA/carboxylated starch in presence of mono-/disaccharides or, poly hydroxy compound. Thermolysis/flame pyrolysis of the precursor mass at external temperatures of around 300–500°C resulted in the oxide phase.

Keywords. Chemical route; nanosized oxides; phosphates; molybdates; tungstate.

1. Introduction

There is a growing need for nanosized mixed-oxide ceramic powders. Often these advanced ceramic materials are tailor made to suit specific applications. Chemical synthesis routes play a crucial role in designing the final product and they are also better and less cumbersome methods for the production of fine-grained mixed-oxide powders. The use of chemistry in the preparation of materials can avoid three major problems—diffusion, impurities and agglomeration. The reasons being that the fine chemically prepared powders allow for shorter diffusion distances and improved homogeneity, the chemical precursors used can be easily refined to increase the purity, and careful control of solvent removal from the precursors will lead to the production of crushable agglomerates.

Over the last few decades, a number of chemical synthesis techniques have been developed for the preparation of nanosized mixed-oxide powders. Most often, the technique begins with the preparation of a precursor solution, in which the ions are well-mixed on a molecular scale. These techniques then employ a variety of methods (such as: spray drying, freeze drying, sol-gel, and coprecipitation) for obtaining the first solid phase from the precursor solution. These solid phases are physical mixtures of crystalline solid intermediate phases (such as oxides, hydroxides, carbonates, oxalates or, cyanides) which are heated to cause decomposition and reaction to the desired multi-component oxide phase (Tseung and Bevan 1973; Anderton and Sale 1979a; Kodogawa and Ikeda 1987; Tejuca and Fierro 1989; Pathak *et al* 1992).

Another group of synthesis techniques seeks to form an amorphous solid intermediate from the liquid precursor. For example, the Pechini (1967) or, amorphous citrate

(Anderton and Sale 1979b; Baythoun and Sale 1982; Lessing 1989; Pramanik 1995) processes which form intermediate amorphous solids that are subsequently decomposed and thermally reacted to form complex oxide phases.

Recently, several variants of self-sustaining combustion synthesis (Ravindranathan and Patil 1987; Chick *et al* 1990; Suresh *et al* 1991) have been developed. Unlike the Pechini or amorphous citrate processes, these self-sustaining combustion processes are rapid and may approach direct conversion from the molecular mixture of the precursor solution to the final oxide product, avoiding formation of intermediate crystalline phases that require interdiffusion for complete reaction.

The chemical methods that have been developed often require a high degree of sophistication and control, in order to obtain the desired characteristic properties in the powders. On the other hand, this invariably increases the cost of products. Hence, the economic aspects of a particular chemical synthesis process needs to be balanced against the possible improvement in the powder characteristics before it could be considered to be commercially viable.

In this paper, we report the preparation of a variety of nanosized mixed-oxide powders from the thermolysis/flame pyrolysis of a new polymer matrix based precursor solution. The precursor solution is constituted of an aqueous solution of the desired metal salts (predominantly, metal nitrates) mixed with the polymer PVA/PAA/carboxylated starch (about 10%) for obtaining the matrix, in presence of aqueous solutions of monosaccharides, or, disaccharides or, poly hydroxy compounds (such as sorbitol, manitol) which acts as the fuel in the process. Over 50 different ceramic oxides have been synthesized using the process and the resulting powders are nanosized

(10–90 nm in diameter), narrow particle size distribution of high purity and are obtained at relative lower pyrolysis temperatures than those reported in literature so far. We believe that the method has great potential for inexpensive manufacture of high quality, ultrafine ceramic oxides.

Considering the huge volume of research work, we will restrict our discussions on the pyrolysis of the precursor solution of metal salts embedded in the polymer matrix provided by PVA, when disaccharide (e.g. sucrose) is used as the fuel in the liquid-mix. The oxide system investigated through this process include (i) pure oxide [e.g. α - Al_2O_3 , Cr_2O_3 , ZrO_2 , ZrO_2 stabilized with 5% $\text{CaO/MgO/Y}_2\text{O}_3$]; (ii) spinels [e.g. MgAl_2O_4 , CuFe_2O_4 , NiFe_2O_4 , CoFe_2O_4 , ZnFe_2O_4]; (iii) orthoferrites [e.g. LaFeO_3 , NdFeO_3 , GdFeO_3 , SmFeO_3]; (iv) garnets [e.g. $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Gd}_3\text{Al}_5\text{O}_{12}$, $\text{Gd}_3\text{Fe}_5\text{O}_{12}$, $\text{Sm}_3\text{Fe}_5\text{O}_{12}$]; (v) nanocomposites [e.g. $\text{Fe}_2\text{O}_3 \cdot \text{NiO}$; $\text{Fe}_2\text{O}_3 \cdot \text{CuO}$; $\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$]; (vi) metal phosphates [e.g. $\text{Co}_3(\text{PO}_4)_2$, $\text{Ni}_3(\text{PO}_4)_2$, $\text{Cu}_3(\text{PO}_4)_2$, $\text{Ba}_3(\text{PO}_4)_2$, AlPO_4 , CrPO_4 , FePO_4]; (vii) metal vanadates [e.g. $\text{Ca}_3(\text{VO}_4)_2$, $\text{Co}_3(\text{VO}_4)_2$, $\text{Ni}_3(\text{VO}_4)_2$, $\text{Cu}_3(\text{VO}_4)_2$, CrVO_4 , FeVO_4 , MnVO_4]; (viii) metal molybdates [e.g. CaMoO_4 , NiMoO_4 , CoMoO_4 , MgMoO_4 , $\text{Sm}_2(\text{MoO}_4)_3$, $\text{Gd}_2(\text{MoO}_4)_3$]; (ix) metal tungstates [e.g. CaWO_4 , MgWO_4 , NiWO_4 , CoWO_4] and (x) aluminates [e.g. LaAlO_3 , SmAlO_3 , NdAlO_3].

2. Experimental

The reported process consists of two basic steps. First, the stoichiometric amounts of the desired metal nitrates, 10% (w/v) aqueous solution of PVA (the matrix) and the aqueous solution of sucrose (the fuel) are mixed together and evaporated to a viscous liquid with the evolution of brown fumes of the decomposed nitrates. The general idea is to distribute the cations atomistically throughout the polymer structure so that selective precipitation is prevented during the evaporation process. Second, the fluffy voluminous carbonaceous pyrolysed mass produced during the complete evaporation of the precursor solution of metal–nitrate–PVA–sucrose is thermolysed/flame pyrolysed (at temperature varying from 300°C to 900°C) to get the nanosized powders of the desired oxide. The details of chemicals required and their mole ratios are given in table 1 for representative sample corresponding to each of the oxide systems studied. The carbonaceous evaporated dry mass (precursor powders) were ground and pyrolysed at various heat-treatment temperatures.

3. Results and discussion

Simultaneously recorded thermal gravimetric (TG) and differential scanning calorimetric (DSC) studies of the evaporated dry carbonaceous mass (hereafter referred to as the 'precursor powder') were carried out in nitrogen

atmosphere with a heating rate of 10°C/min. Figure 1 illustrates the thermogram of $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ precursor powder as a typical example.

The precursor powders may be considered to be constituted of some metal carboxylates (also metal phosphates, vanadates, molybdates, tungstates) and the respective metal oxide trapped in pyrolysed mass produced by the oxidation of PVA and sucrose. The general thermograms reveal a strong exothermic between 300°C and 500°C accompanied by the release of high amount of heat due to the thermal decomposition of trace remaining of metal nitrates and the combustion of the carbonaceous residue from PVA and sucrose. The whole thermal process is accompanied by the evolution of large amounts of gas that is manifested in the high weight loss effects in the TG curve.

The X-ray studies of the precursor and precursor powders after subsequent heat treatment were carried out using Philips PW 1710 X-ray diffractometer with $\text{CuK}\alpha$ radiation and nickel filter. The precursor powders were always found to be X-ray amorphous and the crystalline phases of the desired mixed-oxide system were obtained for heat treatment temperatures ranging between 300 and 500°C. A typical example of the X-ray diffractogram of NiFe_2O_4 system before (i.e. virgin powder) and after heat treatment of the precursor powder is shown in figure 2.

Crystallite sizes for the heat treatment powders were evaluated from the X-ray line broadening studies using the Scherrers' formula (Klug and Alexander 1974). Table 2 shows some of the particle size values of typical oxide system at the indicated heat treatment temperatures.

The particle size measurements for the heat treatment powder were made on CM-12 Philips Transmission Electron Microscope. Some of the values are tabulated in table 2 as typical examples. Typical bright field micrographs of FePO_4 and $\text{Co}_3(\text{VO}_4)_2$ powders heat treated at 500°C are shown as typical representative examples in figure 3.

Figure 1. DSC/TG curves for the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ precursor powders.

In the reported route, nanosized mixed oxides were prepared from the thermolysis of the precursor powders. The process becomes more time efficient if the precursor solution of metal nitrate–PVA–sucrose is boiled down to a honey like consistency and thereafter injected for flame pyrolysis instead of going through the process of slow evaporation of the precursor solution to dry mass. The resultant powders obtained from thermolysis and flame pyrolysis both, may require further heat treatment for obtaining the desired crystalline phase.

The exothermic decomposition of the precursor powder is accompanied by the evolution of large amounts of gases. The evolution of various gases (such as water vapour, CO, CO₂, NO₂, etc) not only helps the precursor material to disintegrate but also to dissipate the heat of decomposition, thus inhibiting sintering of the fine particle. The temperatures of heat treatment significantly influence the reactivity and particle size.

3.1 Role of sucrose in the preparation route

The sucrose in the solution serves two principle purposes. First, it provides a wrapping through coordination for the cations in solution and circumvents their selective precipitation from the solution during the evaporation process. The sucrose, being always in excess to the metal ions, works as a chelating agent and ensures atomistical distribution of the cations throughout the polymeric network structure. The overall reaction can be represented as:

Second, it serves as an efficient fuel for the combustion reaction, being oxidized by the nitrate ions. Stability of the polymeric approach comes from the chemical bonding

Table 1. The details of the chemicals required for the preparative route.

Metal salts/preparation condition	Moles of sucrose (FW-342)	Moles of PVA* (10% w/v aq. solution of PVA)	Total volume of the soln. after mixing
Pure oxide (α Al ₂ O ₃) 1 mole Al(NO ₃) ₃ · 9H ₂ O	2	0.05	1.5 l
Lanthanum aluminate (LaAlO ₃) 0.5 mole La ₂ O ₃ + 3 mole aq. HNO ₃ (75% v/v) + 1 mole Al (NO ₃) ₃ · 9H ₂ O	4	0.05	2.5 l
Y ₂ O ₃ stabilized ZrO ₂ 1 mole NH ₄ OH + 1 mole zirconium oxy-chloride hexahydrate → zirconium hydroxide obtained dissolved in conc. HNO ₃ (1 l) with Y ₂ O ₃ (0.04 mole) dissolved in HNO ₃ (50 cc)	2.5	0.05	2.5 l
Metal phosphate (FePO ₄) Ammonium dihydrogen phosphate (1 mole/ 500 ml H ₂ O) + Fe (NO ₃) ₃ · 9H ₂ O (1 mole in 1 l H ₂ O) + HNO ₃ so that pH = 1	3	0.05	3.0 l
Metal vanadate (YVO ₄) 0.5 mole Y ₂ O ₃ + conc. HNO ₃ (250 ml) produced Y(NO ₃) ₃ solution + vanadyl salt (obtained from 1 mole ammonium vanadate + 4 mole formic acid + 4 mole hydrazine hydrate was slowly added and refluxed for 1 hour at 120°C to produce 1 mole vanadylsalt)	2.5	0.05	2 l
Metal tungstate (CaWO ₄): Freshly prepared CaWO ₄ (1 mole) + ethylene diamine tetracetic acid (1.2 mole) + diethylenetriamine (3 mole) dissolved in 1.5 l water	1	0.05	2 l
Metal molybdate (CaMoO ₄) Freshly prepared CaMoO ₄ (1 mole) + EDTA (1.2 mole) + ethylenetriamine (3 mole) dissolved in 1.5 l water	1	0.05	2 l

*represents the moles of vinyl alcohol monomer units of PVA.

Figure 2. X-ray diffractograms of NiFe_2O_4 precursor and heat-treated powders using CuK_α radiation.

of the cations onto the polymeric chain and from the development of extremely high viscosity polymeric solution. Even as the chemical bonding is destroyed during pyrolysis, the high viscosity favours low cation

Figure 3. Bright field micrographs of powders heat-treated at 500°C for the systems: (a) FePO_4 and (b) $\text{Co}_3(\text{VO}_4)_2$.

Table 2. The average TEM particle size and their respective crystallite size from XRD studies for the various systems at the given heat treatment temperatures.

Sample	Temp. ($^\circ\text{C}$)	Particle size* (nm)	Cryst. size (nm)	Sample	Temp. ($^\circ\text{C}$)	Particle size* (nm)	Cryst. size (nm)
Al_2O_3	900	30–46	26	$\text{Ni}_3(\text{PO}_4)_2$	400	40–85	38
Cr_2O_3	800	30–55	25	$\text{Cu}_3(\text{PO}_4)_2$	400	40–85	35
ZrO_2 , 5%CaO	1100	25–40	28	FePO_4	650	40–90	42
MgAl_2O_3	850	35–55	28	AlPO_4	750	40–80	38
NiFe_2O_4	450	35–60	37	$\text{Ca}_3(\text{VO}_4)_2$	410	65–95	37
CoFe_2O_4	450	35–60	35	$\text{Co}_3(\text{VO}_4)_2$	400	35–65	35
LaFeO_3	600	35–50	32	$\text{Ni}_3(\text{VO}_4)_2$	400	35–60	38
NdFeO_3	600	35–50	33	$\text{Cu}_3(\text{VO}_4)_2$	400	38–78	38
GdFeO_3	600	35–50	35	FeVO_4	480	35–75	34
SmFeO_3	600	35–50	35	CaMoO_4	450		32
$\text{Y}_3\text{Al}_5\text{O}_{12}$	900	25–55	28	NiMoO_4	400		35
$\text{Gd}_3\text{Al}_5\text{O}_{12}$	900	30–65	30	$\text{Gd}_2(\text{MoO}_4)_3$	480		29
$\text{Gd}_3\text{Fe}_5\text{O}_{12}$	800	35–70	35	CaWO_4	440		37
Fe_2O_3 , 0.5 Mn_2O_3	400	80		MgWO_4	440		35
Fe_2O_3 , 0.5 CuO	400	80		NiWO_4	400		42
NiCr_2O_4	450	40–80	35	CoWO_4	400		44
CuCr_2O_4	400	40–85	35	LaAlO_3	650	40–50	42
Cr_2O_3 , 0.5 CuO	700	65		SmAlO_3	650	45–65	45
$\text{Co}_3(\text{PO}_4)_2$	400	40–85	38	NdAlO_3	650	45–65	42

*The TEM particle sizes varied within the limit of ± 5 nm

mobility which helps affect the crystallite/agglomerate morphology.

The aqueous solution of sucrose in presence of dilute nitric acid gets hydrolyzed to fructose and glucose that gets further oxidized to gluconic acid (or, a poly hydroxy acid).

The gluconic acid has a carboxylic acid group in one end and five linear hydroxy groups, which can participate in the complexation of metal ions and it may form branched polymer with PVA. It is observed that sucrose only in presence of PVA, in very small quantity (at 10%) gave rise to crushable, fluffy powder of the oxide system. And it was an empirical observation that the higher the fluffiness of the powders lower was the particle size.

The PVA provides a polymeric matrix structure for the cations and also provides heat through combustion of the carbonaceous material remaining of oxidized PVA. In addition, it helped in the polycondensation reaction in presence of oxidized saccharides and gave rise to a branched chain polymer network structure where the metal ion (M^{+x}) were held in the hydroxylic pockets of the branch chain through complex formation. During pyrolysis of these branched chain polymer would release various gases from the pocket making the structure highly porous and fluffy. To substantiate the hypothesis, we performed the experiment with prepolymeric material from gluconic acid and PVA that produces the nanosized oxides very efficiently due to the efficient chelation from branched chain.

For the cases of phosphates, vanadates, molybdates, tungstates, to inhibit the immediate precipitation, EDTA was added to form stable complexes and counter ions e.g. PO_4^{3-} , VO_4^{3-} , MoO_4^{2-} , WO_4^{2-} remained in the solution as a organoammine and complex of tungstate or molybdate has poor solubility in the complex-recipe mixture.

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