Research Article

Microwave-Assisted Synthesis of Mixed Metal-Oxide Nanoparticles

Akrati Verma, 1 Reena Dwivedi, 1 R. Prasad, 1 and K. S. Bartwal 2

1 School of Chemical Sciences, Devi Ahilya University, Indore 452001, India
2 Laser Materials Development & Devices Division, RRCAT, Indore 452013, India

Correspondence should be addressed to K. S. Bartwal; bartwalks@yahoo.co.in

Received 21 January 2013; Accepted 9 February 2013

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Nanoparticles of mixed metal oxides, ZrO 2 , ZrTiO 4 , and ZrV 2 O 7 were prepared by microwave-assisted citrate sol-gel and solution combustion method. The prepared nanoparticles were characterized for their structural details using XRD and TEM techniques. The broadening of Raman bands is ascribed to local compositional fluctuations or local positional disordering produced due to random distribution of Zr 4+ and Ti 4+ between equivalent sites. The XPS spectra confirm the incorporation of Ti in ZrO 2 and suggest Zr as well as Ti in +4 oxidation state. Gelation and fast combustion seem to be the reason for smaller particle sizes. ZrV 2 O 7 nanocrystalline material was synthesized by microwave-assisted solution combustion method. Low angle powder XRD measurements confirm the mesoporous nature of the prepared material. The effect of calcination temperature on the phase transformation of the materials has been investigated. Among tetragonal, monoclinic, and cubic phases, the monoclinic phase is predominant at higher calcinations temperature. The XPS confirms the incorporation of V 2 O 5 in ZrO 2 and suggests that Zr and V are in the same oxidation state (+4). The average particle sizes for ZrO 2 , ZrTiO 4 , and ZrV 2 O 7 were found to be in the ranges of 5–10 nm, 2–5 nm, and 10–50 nm, respectively.

1. Introduction

Combination of two metal oxides M 1 O and M 2 O can be either a simple mechanical mixing involving weak van der Waals forces or a chemical possessing chemical linkages of the type M 1 –O–M 2 . The physicochemical properties of the latter combination will be entirely different from the simple combination of individual oxides (mechanical mixture). The degree of dispersion in the chemical route depends on preparation method and synthetic conditions. Because of this, many different synthetic routes for mixed metal oxides have been developed. Some of the popular routes for preparation of mixed oxides are coprecipitation, sol-gel method, condensed phase combustion, and microwave-assisted solution combustion method.

Copprecipitation (wet precipitation) is the most widely used method for oxide synthesis. In this method hydroxide of the metals is precipitated from an aqueous solution of the metal salt by titrating it with ammonia solution. The hydroxide is washed, dried, and calcined to get the metal oxide. Sol-gel method is used to prepare metal oxides by hydrolysis and condensation of metal alkoxides M(OR) 2:

\[ M(OR)_2 + x\text{HOH} \rightarrow M(OR)_{2-x}(\text{OH})_x + x\text{ROH} \] (1)

The reaction follows an SN 2 mechanism in which the nucleophile OH - adds to the M + and increases its coordination number in the transition state:
The $H^+$ changes its position to alkoxy group producing a protonated ROH species which is subsequently eliminated, and metal hydroxide is produced. Production of MgO is a typical example. The rate of hydrolysis and condensation depends on (1) electronegativity of the metals atom, (2) ability of the metal atom to increase its coordination number, (3) steric hindrance of the alkoxy group, (4) solvents, (5) molecular structure of the metal alkoxide, (6) hydrolysis ratio $h = H_2O/Metal$, and (7) catalyst. The rate of hydrolysis of $Ti(OEt)_4$ is $10^7$ times faster than that of $Si(OEt)_4$. This can be attributed to the ability of $Ti$ to expand its coordination number from 4 to 6. For the same reason the hydrolysis of $Sn(OR)_4$ is much faster compared to $Si(OR)_4$.

Most advanced ceramics are multicomponent systems having two or more types of cations in the lattice. It is therefore necessary to prepare gels of high homogeneity in which cations of various kinds are distributed uniformly at an atomic scale through M-O-M bridges. A major problem in forming homogeneous multicomponent gel is the unequal hydrolysis and condensation rates of the metal alkoxides. This may result in chemical inhomogeneities, leading to higher crystallization temperatures or even undesired crystalline phases. Several approaches have been attempted to overcome this problem including partial prehydrolysis of less reactive precursors, matching of hydrolysis rates by chemical modification with chelating ligands, and synthesis of heterometallic alkoxides. Conventional self-propagating high temperature synthesis (SHS) or condensed phase combustion is associated with difficulties like large particle size of nanomaterials and high reaction temperature of about 2000°C. Combustion of metal oxides by Mg in the presence of NaCl produces small particles of metals coated with NaCl. Subsequent treatment of the powder with dilute acid removes MgO impurity. Metal can be recovered by washing the sample with water.

Microwave-assisted method of oxide synthesis is gaining popularity because of its high rate of reaction, efficient heat transfer, and environmental friendly nature. In this process material is directly heated by radiation instead of indirect heating by thermal sources leading to higher temperature homogeneity in the reaction mixture. In this process of heating, microwave radiation interacts with the polar molecules possessing dipole moment and makes them reorient through rotation. A large number of molecules try to orient together resulting in collision and production of heat. Thus microwave heating is energy conversion method in which electromagnetic radiation is converted into heat energy rather than heat transfer by convection in conventional heating. In microwave-assisted solution combustion synthesis (MWSCS) an aqueous solution of metal nitrate (oxidant) and fuel (urea, citric acid) is subjected to a microwave heating for few minutes to obtain a viscous gel which on drying and calcination produces the metal oxide/mixed metal oxide. The solution combustion method seems to be modification of the conventional oxalate method which is used for preparing metal oxides and supported metal oxides. The citrate gel decomposition process is better known as a thermally induced anionic oxidation-reduction reaction. In the process chelates are formed between metal ions facilitating atomic scale distribution of ions in a polymer network. Heating of this resin causes the breakdown of the polymer, and a solid amorphous precursor material is finally obtained. On subsequent heating between 500 and 900°C, the cations are oxidized to form the respective metal oxides. Microwave-assisted MVSCS technique can be used for preparing materials or catalysts, catalyst support, fuel cells, capacitors, Li-ion rechargeable batteries, dye-sensitized solar cells, solid oxide fuel cells (SOFC), and direct methanol fuel cells (DMFCs).

The development of zirconia ($ZrO_2$) nanoparticles has attracted much attention due to their multifunctional characteristics. Nanoparticles have been recognized to have potential in the area of photonic applications. It has several applications such as solid oxide fuel cell, biosensors, $H_2$ gas storage material, oxygen sensor, catalyst, and catalyst support [2–5]. In addition, zirconia is used as piezoelectric material, electrooptic material, and dielectric material [6–8]. It is also used as support to disperse various noble and transition metals for distinct catalytic applications. Zirconia is a well-known solid acid catalyst and an n-type semiconductor material. $ZrO_2$ is also used as toughening ceramics in thighbone and oral planting [9]. The existence of metastable tetragonal (t-$ZrO_2$) at low temperature has been synthesized by several methods. Some of the methodologies such as oxidation of $ZrCl_4$ by molecular oxygen [10], molten hydroxides method [11], nonhydrolytic sol-gel reaction between isopropanoxide and $ZrCl_4$ [12], and sol-gel template technique [13, 14] are developed to prepare nanocrystalline $ZrO_2$.

The traditional preparation of zirconium titanate ($ZrTiO_4$) ceramic is based on solid-state reaction between the $TiO_2$ and $ZrO_2$ powders at high temperatures (above 1400°C) [15]. In order to improve the functional properties of the ceramic material, heat treatments are generally necessary which consume high amount of energy. Chemical method based on Coprecipitation of the reactive precursors was developed to prepare powders with a high purity and low treatment cost after reaction [16]. Low temperature synthesis of zirconium titanate has been reported by Karakchiev et al. [1] and Dos Santos et al. [17]. Zirconium titanate possessing a layered wolframite-type structure ($ABO_4$) with space group $P2_1$ finds applications as microwave components. As catalyst and catalyst supports, $ZrTiO_4$ is employed for a wide variety of catalytic applications both in liquid and gaseous phases [18, 19]. Recently it has been reported that the oxide nanoparticles are promising for photonics, and their monodispersion and appropriate contact with the surrounding medium are very crucial parameters [20, 21].

Vanadium incorporated zirconia ($V_2O_5$-$ZrO_2$) is a mesoporous material and is very useful catalyst. Nanoporous materials consist of a regular organic or inorganic framework supporting a regular, porous structure. A mesoporous material is a material containing pores with diameters between 2 and 50 nm. The α-phase (cubic) of $ZrV_2O_7$ is the stable structure at ambient conditions. It consists of $ZrO_6$ octahedra whose corners share their oxygen atoms with $VO_4$ tetrahedra. Vanadium oxide catalysts supported on different metal oxides are widely used in many industrial reactions, such as selective catalytic reduction of NO with NH$_3$, ammoniation of alky aromatics, and the selective oxidation of hydrocarbons. Properties of supported vanadium catalysts depend on a variety
of factors, such as percentage of vanadium loading, method of preparation interaction, and nature of the support [22]. Various supporting oxides used for vanadium loading include Al₂O₃, TiO₂, SiO₂, ZrO₂, MgO, and HfO₂ [23, 24]. Among all these oxides, ZrO₂ is a better choice as it interacts with vanadium relatively strongly, preventing its sintering, and helps in producing highly dispersed vanadium on ZrO₂. Besides, ZrO₂ is thermally and chemically stable at the different reaction conditions. Solution combustion synthesis is a versatile, low-cost, simple, and rapid process, which allows effective synthesis of a variety of nanosize materials. This process involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine, and hydrazides) [25, 26].

The objective of the present work is to synthesize zirconium oxide, zirconium titanate, and zirconium vanadate nanocrystalline powder by microwave-assisted method. The combustion synthesis for preparing ZrO₂ has been performed under microwave using citric acid as fuel and zirconium oxychloride as oxidizer. The ZrTiO₄ particles were prepared using titanyl nitride and zirconium oxychloride as precursors. The ZrV₂O₇ nanoparticles were synthesized by microwave-assisted solution combustion method. The prepared nanoparticles were characterized for their structure-property relationship. The particle size and crystalline phase of the catalysts were determined by powder X-ray diffraction (XRD). The TEM technique was used to confirm the formation of single phase material with nanocrystalline particles. Raman and XPS spectroscopy techniques were used to characterize the structure and electronic properties. The present problem was undertaken with an aim (1) to develop a versatile, effective, low-cost, simple, and fast solution combustion assisted method for synthesis of these zirconia-based oxide nanoparticles and (2) to characterize the prepared nanoparticles by employing various physicochemical methods.

2. Experimental Details

Zirconia (ZrO₂) nanoparticles were prepared by citrate sol-gel method. High purity chemicals, zirconium oxychloride (S.D. Fine Chemicals), and anhydrous citric acid (LOBA Chemie Pvt. Ltd.) were used as precursors. In the present set of experiments, 9.78 g of zirconium oxychloride (ZrOCl₂·8H₂O) was mixed with 7.68 g of citric acid (C₆H₈O₇·H₂O) in a 250 mL corning glass beaker. Demineralized water was added to have homogeneous slurry of pH 2. The solution was evaporated to dryness by exposing it to microwave for 2 min. The material swells into a white colored gel. The product obtained was ground and kept for calcination in a tubular furnace at a temperature of 450°C for 4 h. On calcinations a black colored residue was obtained which was ground in a motor pastel to make a fine powder. Similarly, zirconium titanate (ZrTiO₄) nanoparticles were prepared by citrate sol-gel method. Zirconium oxychloride, anhydrous citric acid, and titanyl nitrate were used as starting materials. The titanyl nitrate was prepared by reacting tetrabutyl orthotitanate with nitric acid and evaporating the resulting mixture to dryness. The replacement of Zr by Ti was optimized, and two sets of compositions in Zr: Ti ratio, 1:0.1 and 1:1, were prepared. In a typical preparation, 3.2 g of ZrOCl₂·8H₂O, 0.29 g of titanyl nitrate, and 3.5 g of citric acid were used for 1:0.1 ratio of Zr: Ti (named ZT1), and 3.2 g of ZrOCl₂·8H₂O, 2.95 g of titanyl nitrate, and 6.15 g of citric acid were used for the 1:1 ratio of Zr: Ti (named ZT2). These precursors were mixed in a 250 mL corning glass beaker, and enough demineralized water was added to have homogeneous slurry of 2 pH. The well-mixed solution was evaporated to dryness by exposing it to microwave for 2 min. This step of drying in microwave oven was optimized, and the time of 2 min was found suitable for this composition. The dried material was ground and kept for calcination in a resistive heating tubular furnace at a temperature of 400°C for 4 h. A grayish colored residue was obtained on calcination which was again ground in a motor pastel to make a fine powder. Both compositions of ZrTiO₄ with Zr: Ti ratio 1:0.1 and Zr-Ti ratio 1:1 were prepared with the same procedure in similar conditions. These samples were named as ZT1 and ZT2, respectively, and were used for various physicochemical studies.

Mesostructured vanadium oxide supported on zirconium oxide was synthesized by microwave-assisted solution combustion method [25, 27]. Zirconium oxychloride (S.D. Fine Chemicals) and ammonium metavanadate and urea (LOBA Chemie Pvt. Ltd.) were used as starting materials. In a typical preparation of 10% vanadium doped zirconia (ZV10), a solution of zirconium nitrate (prepared by mixing 5.8 g of zirconium oxychloride with 12 mL of 1:2 HNO₃) is mixed with another solution prepared by mixing 0.23 g of NH₄VO₄ in 50 mL of water. The final solution was mixed with 1.2 g of urea and fired in a muffle furnace at 200°C for 15 min. The material swells into a yellow colored gel. The product obtained was ground and kept for calcination in a tubular furnace at a temperature of 400°C for 4 h. On calcination a green colored residue was obtained. The prepared powder was ground several times before putting it in specimen holder to minimize the possible preferred orientation effects. For the preparation of all the ZVₙ materials, 1:1 molar ratio of urea to metal oxide (Zr + Vₙ) was taken. Four different samples with varying VₙO₇ concentrations were prepared. The samples were named according to VₙO₇ concentrations of 2, 5, 8, and 10 mol% and named as ZV2, ZV5, ZV8, and ZV10, respectively.

The crystallite sizes and structural morphology were investigated by transmission electron microscopy (TEM) in high-resolution mode. Philips make, Tecnai G²−20 (FEI) electron microscope operating at 200 kV was used for TEM experiments. Sample for TEM observation was prepared by suspending the particles in ethanol by ultrasonification and drying a drop of the suspension on a carbon coated copper grid. Raman spectrum in the range 50–4000 cm⁻¹ was recorded using Labram HR 800 micro-Raman spectrometer with 488 nm wavelength Ar⁺ laser source at the energy of 2.53 eV with recording time of 10 sec. The core level X-ray photoelectron spectroscopy (XPS) spectra of ZrTiO₄ and ZrV₂O₇ were measured using Omicron Nanotechnology (EA1-25) photoelectron spectrometer with Al Kα radiation (E = 1486.6 eV) as excitation source. The base pressure of the analysis chamber of the system was less than 5 × 10⁻¹⁰ mbar.
during the experiments. Energy scale of the spectrometer was calibrated by setting the measured Au 4f$_{7/2}$ and Cu 2p$_{3/2}$ binding energies to 84.00 ± 0.05 and 932.66 ± 0.05 eV, respectively, with regard to $E_F$. The energy drift due to charging effects was calibrated taking the XPS, C1s (285.0 eV) core-level spectrum of hydrocarbons.

3. Results and Discussion

It is known that the main crystal phases of ZrO$_2$ are cubic (c), tetragonal (t), and monoclinic (m). The IR frequencies for cubic, tetragonal, and monoclinic phases are 480, 435, and 270 cm$^{-1}$, respectively. This indicates that phonon energy of the ZrO$_2$ host varies in the crystal phases. The monoclinic phase is thermodynamically stable up to 1100°C, the tetragonal phase exists in the temperature range 1100–2370°C, and the cubic phase is found above 2370°C. The nanoparticle of tetragonal zirconium oxide (t-ZrO$_2$) were prepared by microwave-assisted citrate sol-gel technique. Zirconium titanate, ZrTiO$_4$, with two different Zr : Ti ratios was prepared to understand the complete replacement of Zr ion by Ti. The Zr : Ti ratios taken were 1:0.1 (ZT1) and 1:1 (ZT2). These samples were prepared by microwave-assisted citrate sol-gel method. The microwave was used during the sol-gel drying process to make the particles more homogeneous in Zr/Ti ionic ratio. The prepared samples were subjected to various characterization studies to understand dispersion of Ti ions and the role of microwave in preparation. Zirconia supported vanadate (ZrV$_2$O$_7$) was synthesized by microwave-assisted solution combustion method. The two-dimensional vanadia species with tetrahedral coordination appear on the surface of the ZrO$_2$ and expand in size with increasing V$_2$O$_5$ concentration. ZrV$_2$O$_7$ is formed as a consequence of zirconia migration into the V$_2$O$_5$ crystallites. The prepared nanoparticles were found having mesoporous structure. The structures of the zirconia support and of the dispersed vanadia were characterized. The prepared nanoparticles were investigated for their phase and structure by powder XRD using Cu K$_\alpha$ radiation ($\lambda = 1.5406$ Å, Rigaku Geiger Flex X-ray diffractometer). The powder XRD data were collected in the 2$\theta$ range from 20 to 80 degrees with the scan rate of 2° per minute.
structural modifications known for this system are high-temperature disordered \( Zr_{1-x}TiO_4 \) (Ti-excess) and low-temperature ordered \( ZrTiO_4 \). The XRDs for the samples ZT1 and ZT2 are reproduced in Figure 1(b), which indicate the formation of \( ZrTiO_4 \) orthorhombic phase, which is closely matching with JCPDS file no. 34-415. To a first approximation, this major phase has orthorhombic structure of \( a-PbO_2 \) with space group \( Pbnm \), with the cell parameters \( a = 4.80 \, \text{Å}, \ b = 5.49 \, \text{Å}, \) and \( c = 5.03 \, \text{Å} \). Most of the peaks for the samples ZT1 and ZT2 are matching, the only difference being the intensity of the peaks which is different for Zr-rich composition (ZT1). The diffraction characteristic peaks for this phase were obtained with the \( (h \, k \, l) \) values of (011), (111), (200), (220), (022), and (311). The doublets observed in the XRD pattern for \( ZrTiO_4 \) at 2\( \theta \) values 35, 37, and 54 are due to the presence of small amount of secondary phase \((Zr_4Ti_2O_{24})\) of Ti-rich phase in \( Zr-Ti \) system. It has been known that some small amounts equation of \( ZrO_2 \) and \( TiO_2 \) are also expected to be formed during the process. The average particle size was calculated from (111) diffraction peak using Scherrer’s, and the average particle size was calculated to be 4.8 nm for ZT1 and ~6.14 nm for ZT2.

XRD pattern for pure \( ZrO_2 \) material calcined at 400°C and 10 wt% \( V_2O_5 \) supported on \( ZrO_2 \) calcined at different temperatures in the range of 20°–70° is shown in Figure 1(c). The pattern has been indexed with the tetragonal \( ZrO_2 \) (JCPDS card no. 81-1551) and cubic \( ZrV_2O_7 \) (JCPDS card file no. 16-0422). The absence of vanadia or vanadate peaks (2\( \theta \) = 20.3° and 26.2°) in the sample calcined at 400°C and 600°C can be noticed. The appearance of the vanadia peaks in the samples calcined at 800°C is clearly seen. The presence of these peaks with lower intensity in the sample calcined at 800°C confirms that the vanadium ions have occupied the zirconium ions at their lattice positions and high dispersion of vanadia ions on zirconium oxide surface [29]. On calcination at higher temperatures the full width at half maximum of the diffraction peaks decreases. This decrease in FWHM suggests that the sizes of prepared zirconium vanadate nanoparticles are increasing at higher temperatures. When zirconium vanadate sample was calcined at 400°C and 600°C, a very sharp peak appeared at 30.34° which can be ascribed to tetragonal phase. On calcination at 800°C, two sharp peaks appeared at 28.2° and 31° which is ascribed to the monoclinic phase of \( ZrO_2 \) [30]. The average particle size was calculated from (111) diffraction peak using Scherrer’s equation and the average particle size was calculated to be 16 nm, 27 nm, and 49.63 nm, respectively, for 10 wt% zirconium vanadate samples calcined at 400°C, 600°C, and 800°C. Low angle powder XRD pattern of the prepared nanoparticles calcined at 400°C for 4 h was recorded in order to explore structural feature of zirconium supported mesoporous vanadium materials. Figure 2 shows the low angle powder XRD pattern. The appearance of peak in low angle region at 0.3° confirms the mesoporous nature. It has been known that the presence of sharp peak in low angle region confirms the disordered wormhole type mesoporosity in \( ZrV_2O_7 \) [31]. The increase in the intensity of the peak present at 0.3°, with increasing V concentration, suggests the enhancement in mesoporosity in the material.
Transmission electronic microscopy (TEM) in high-resolution mode is the best tool to analyze the morphology and the sizes of the prepared nanoparticles [32–34]. Figures 3(a) and 3(b) show the representative TEM micrographs taken for the ZrO$_2$ samples calcined at 450°C. The corresponding selected area electron diffraction (SAED) patterns are inserted into the micrographs. Figure 3(a) shows a typical TEM image for the dried powders. The powders are very fine and agglomerated. Electron diffraction analysis reveals that they have amorphous characteristics due to small particle sizes. The micrograph shown in Figure 3(a) indicates the formation of nanoparticles with sizes ranging from few nanometers to few tens of nanometers. The corresponding diffraction pattern shows few clear spots along with connecting diffraction rings. The presence of spots along with the streaks shows the presence of crystallite of reasonably sufficient sizes to diffract. The connecting streaks indicate the short-range order due to presence of some smaller size particles as well. The high-resolution electron micrograph for the samples annealed at 450°C is shown in Figure 3(b). The clarity in the fringe patterns inside the crystallite indicates the formation of single phase ZrO$_2$ with the long-range order in the structure. The corresponding SAED pattern is inserted into the micrograph. The clear spots in SAED pattern suggest that the crystallites are of sufficiently large size. The absence of rings in the SAED pattern is indicative of the crystalline order, larger particle size, and long-range order in the crystallites. The TEM results also suggest the successful preparation of tetragonal phase of ZrO$_2$ nanocrystals with the crystallite sizes ranging $\sim$5–10 nm.

The samples of ZrTiO$_4$ (ZT2) with the Zr:Ti ratio of 1:1 calcined at 400°C were also analysed using TEM, and the micrographs taken are shown in Figures 4(a) and 4(b). Corresponding selected area electron diffraction (SAED) patterns are inserted into the micrographs. The micrograph shown in Figure 4(a) shows the formation of nanoparticles. The SAED pattern inserted into the micrograph shows the few sharp spots along with connecting diffuse rings. The smaller size particles are responsible for the connecting rings which suggests the short-range order. The high-resolution electron micrograph (HRTEM) for the sample ZrTiO$_4$ (ZT2) is shown in Figure 4(b). The fringe patterns indicate the formation

Figure 3: (a) Representative TEM micrograph for ZrO$_2$ sample annealed at 450°C. (b) High-resolution TEM micrograph for samples annealed at 450°C. The corresponding SAED patterns are inserted into micrographs.

Figure 4: (a) Representative TEM micrograph for ZrTiO$_4$ sample. (b) High-resolution TEM micrograph for the same sample. The corresponding SAED patterns are inserted into micrographs.
of single phase ZrTiO$_4$ with the long-range ordering in the structure. The corresponding SAED pattern is inserted into the micrograph. Spots along with rings in the SAED pattern suggest the larger particle size and short-range order in the crystallites. These results on TEM suggest the preparation of the desired phase of ZrTiO$_4$ nanocrystals with the crystallite sizes ranging $\sim$2–5 nm.

The high-resolution TEM images and corresponding selected area electron diffraction (SAED) patterns for ZrV$_x$O$_{7-x}$ samples (ZV8 and ZV10) calcined at 400$^\circ$C are shown in Figures 5(a) and 5(b). HRTEM micrograph shown in Figure 5(a) confirms the formation of nanoparticles with varying sizes. The particle sizes are in $\sim$20–30 nm range and sufficient to diffract and produce SAED pattern. The SAED diffraction pattern inserted into the micrograph (Figure 5(a)) shows the presence of sharp spots along with diffuse spots and connecting ring. The position of the reflections (shown by arrow) in the electron diffraction pattern and broadening of the rings indicate the presence of small randomly oriented V-Zr mixed oxide particles. The HRTEM for ZV10 shown in Figure 5(b) shows that the particle sizes increase with increasing V concentration. Sharp and clear spots along the SAED pattern in Figure 5(b) suggest the long-range order between the crystallites. The particle sizes are in $\sim$20–50 nm range and sufficient to diffract and produce sharp and clear SAED pattern compared to ZV8. The previous TEM results of diffraction and high-resolution mode suggest the successful preparation of the cubic ZrV$_x$O$_{7-x}$ nanoparticles with the particle sizes ranging $\sim$20–50 nm. The TEM results show that there is no secondary phase formation due to vanadia separation. The formation of well-crystallized ZV nanoparticles is clearly seen in the micrographs. The particle size of the as-prepared materials was found to increase with the increase in the V concentration.

It has been known that the Raman spectroscopy can be used to determine the symmetry of a crystal system for oxide materials as it is very sensitive to the polarizability of the oxygen ions. In fact Raman spectroscopy is a technique more sensitive to short-range order than X-ray diffraction, and it can show the peaks for anatase or rutile as well as monoclinic zirconia along with that of tetragonal zirconia. Raman spectroscopy has been performed on all the nanocrystalline samples of ZrO$_2$ and ZrTiO$_4$ samples. The Raman spectra of ZrO$_2$ calcined at the temperatures of 600$^\circ$C and 800$^\circ$C are plotted in Figure 6(a). The assignment of the observed bands was made on the basis of the comparison of the observed spectra with those of reported in the literature [1, 35, 36]. The vibrational Raman active modes are classified as

$$\Gamma = A_{1g} + 2B_{1g} + 3E_g.$$  \hfill (4)

In $A_{1g}$ mode oxygen atoms move in the $z$-direction only. The $B_{1g}$ modes also involve motion in the $z$-direction; however now both Zr and O atoms participate. In $E_g$ modes, Zr as well as O atoms move in the $x$-$y$ plane. In Figure 6(a), the plot (A) represents the Raman spectra for the sample calcined at 400$^\circ$C. The band that appeared at 643 cm$^{-1}$ can be assigned to $A_{1g}$ mode since it involves movement of two oxygen atoms only and is expected to appear at higher wavenumber. The next two bands that appeared at 470 and 382 cm$^{-1}$ are assigned to doubly degenerate $E_g$ modes on the simple reasoning that these two modes also do not involve movement of Zr atoms. The remaining three modes, namely, two $B_{1g}$ modes and one $E_g$ modes are assigned to the remaining three bands appeared at 259, 146, and 123 cm$^{-1}$, respectively. The spectrum of sample calcined at 600$^\circ$C is shown as curve (B) in Figure 6(a). The previous bands that appeared in the Raman spectra for both samples are assigned to t-ZrO$_2$. In addition, few faint bands at 563, 536, 381, 293, and 176 cm$^{-1}$ have appeared which are due to the coexistence of small amount of monoclinic phase.

The Raman spectra of ZrTiO$_4$ (ZT1 and ZT2) are shown in Figures 6(b) and 6(c). The location of band positions is shown in Table 1. The band positions recorded by Karakhchiev et al. [1] for ZrO$_2$ are shown in Table 1 for comparison. ZrTiO$_4$ with orthorhombic symmetry (space group Pbca, point group mmm) and two formula units in a unit cell have 33 optically active modes of vibration, 18 of which are Raman active and 15 are infrared active phonon modes. Their distributions are as follows: Raman: $4A_g$, $5B_{1g}$, $4B_{2g}$,
Figure 6: Raman spectra of (a) ZrO$_2$ precipitated at pH 2 and calcined at different temperatures, (b) ZT1 and (c) ZT2 calcined at 400°C, and (d) ZV10 calcined at (A) 400°C, (B) 600°C, and (C) 800°C.

The band positions are at lower wavenumbers, bands are too weak to be observed, bands are hidden due to overlap by other bands, and lower degree of ordering in nanocrystalline ZrTiO$_4$. The bands due to that appeared in nanocrystalline ZrTiO$_4$ samples are broader compared to those in ZrO$_2$ and can be attributed to local compositional fluctuations or local positional disordering produced due to random distribution of Zr$^{4+}$ and Ti$^{4+}$ between equivalent sites in the crystal lattice.

In the similar experimental setup, the representative Raman spectra for ZrV$_2$O$_7$ (ZV10) samples calcined at 400°C, 600°C, and 800°C are plotted in Figure 6(d), and the assignments of bands are made on the basis of reported assignments [1, 35–39] and are given in Table 2. 14 Raman-active modes centred at 144, 176, 187, 269, 282, 384, 406, 474, 654, 705, 773, 889, 996, and 1044 cm$^{-1}$ were detected. The ZrV$_2$O$_7$ crystals contain the VO$_4$ tetrahedra and ZrO$_6$ octahedra in the structure. The modes centred at 889, 996, and 1044 cm$^{-1}$ are assigned to symmetric stretching of the VO$_4$ tetrahedra.
The modes centred at 705 and 773 cm\(^{-1}\) are assigned to the asymmetric stretching of the VO\(_4\) tetrahedra. The modes centred at 269, 282, and 384 cm\(^{-1}\) are assigned to the symmetric ZrO\(_6\) octahedral stretching and at 406 cm\(^{-1}\) to the asymmetric ZrO\(_6\) octahedral bending. The modes centred at 474 and 654 cm\(^{-1}\) are assigned to ZrO\(_2\) tetragonal stretching. The low frequency bands that appeared at 144, 176, and 187 cm\(^{-1}\) are assigned to lattice vibrations. The sharpness in the peaks is observed with the increase in calcination temperature indicating increase in particle size with temperature. These results are consistent with previous studies of V\(_2\)O\(_5\)/ZrO\(_2\) which have also confirmed the formation of ZrV\(_2\)O\(_7\) on calcination at high temperatures [40, 41].

X-ray photoelectron spectroscopy (XPS) method has been used to study experimentally the valence-band and core-level spectra as well as the energy distribution of some occupied valence states of the constituent atoms of ZrTiO\(_4\). The XPS spectra show that the XPS bands for Zr 3d, Zr 3p, and Ti 2p core-level spectra are simple spin doublets with the XPS Zr 3d\(_{5/2}\), Zr 3p\(_{3/2}\), and Ti 2p\(_{3/2}\) core-level binding energies appearing at 190, 342, and 440 eV, respectively, which correspond to those of titanium and zirconium in the formal valence state of Zr\(^{4+}\) and Ti\(^{4+}\) [43]. The previous results reveal that in ZrTiO\(_4\) the binding energy positions of Ti 2p and O 1s core levels match well with the reported values. Similarly, the XPS of ZrV\(_2\)O\(_7\) was taken using UHV analysis system with Al K\(\alpha\) radiation (\(E = 1486.6\) eV) and hemispherical analyzer operating at constant pass energy of 25 eV being used as a source of XPS spectra excitation. Figure 7(b) shows the XPS survey spectrum of ZrV\(_2\)O\(_7\). The spectrum confirm the presence of vanadium, zirconium, carbon, and oxygen [42, 44]. The peak at 517 eV is due to V 2p\(_{3/2}\) and indicates the presence of V\(^{5+}\) species. The peak that appeared at 524.4 eV can be assigned to V 2p\(_{1/2}\) and shift in this peak from 523 eV to 524.4 eV can be ascribed to change in the oxidation state from V\(^{4+}\) to V\(^{5+}\). The strong peak that appeared at 537.6 eV is assigned to O 1s. The peak at 291.5 is due to C 1s, and
the doublet that appeared at 340.1 eV and 353.3 eV can be assigned to Zr 3p\(_{3/2}\) and Zr 3p\(_{1/2}\), respectively. The binding energy positions of the species (V, O, and Zr) obtained in the present investigations match well with the reported values.

4. Conclusion

Microwave-assisted method of oxide synthesis is important due to its high reaction rate, efficient heat transfer, and environmentally friendly nature. In this process material is directly heated by radiation leading to higher temperature homogeneity. Zr\(_2\)O\(_7\) and Zr\(_2\)TiO\(_4\) nanoparticles were synthesized by microwave assisted citrate sol-gel method. Nanoparticles of V\(_2\)O\(_3\) supported on ZrO\(_2\) were synthesized by microwave-assisted solution combustion method. The formation of tetragonal crystalline phase (t-ZrO\(_2\)) was confirmed by powder XRD analysis. The low angle powder XRD measurements confirm the mesoporous nature of Zr\(_2\)V\(_2\)O\(_7\) and formation of single phase material up to 10 wt% of vanadium incorporation. The morphology, particle size, and microstructure were analyzed using high-resolution transmission electron microscopy. The HRTEM data also confirms the formation of single phase t-ZrO\(_2\). Raman spectra further support and confirm the crystalline phase as well as the specific bands to show the modes of vibration in Zr-O system, whereas the specific bands indicate the modes of vibration in Zr-Ti-O and ZrV\(_2\)O\(_7\) systems. The XPS results show that the X-ray emission of Ti I\(_{\alpha}\), Zr I\(_{\alpha,15}\), and O K\(_{\alpha}\) bands on a common energy scale indicates that Ti 3d, Zr 4d, and O 2p states contribute throughout the valence-band region of ZrTiO\(_4\). The Raman spectra show the specific bands indicative of the modes of vibration in Zr-V-O system and presence of VO\(_4\) tetrahedra and ZrO\(_6\) octahedra in the crystal structure. XPS results show that the X-ray emission of V, Zr, and O bands on a common energy scale indicates that V 2p, Zr 3p, and O 1s states contribute throughout the valence-band region. The crystallite sizes were found to be in the ranges of \(~5–10\ nm, \sim2–5\ nm, and \~20–50\ nm for ZrO\(_2\), ZrTiO\(_4\), and ZrV\(_2\)O\(_7\), respectively.

References


