# High-quality zirconia powder resulting from the attempted separation of acetic acid from acrylic acid with zirconium oxychloride

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Both acetic and acrylic acids are low molecular weight carboxylic acids with very similar physical and chemical properties. As a result it is difficult to separate these two acids by the now commercially significant separation techniques such as distillation, solvent extraction, adsorption, ion exchange, calcium salt precipitation, and membrane processes. We propose a metal–organic precipitation process using zirconium oxychloride to separate acetic acid from acrylic acid in the effluent of an acrylic acid plant. The process developed is based on the selective precipitation of acrylic acid, at suitable pH values, by the addition of zirconium oxychloride to the effluent. The resulting precipitate is a precursor that can yield a pure, ultrafine, and partially-stabilized zirconia powder which has been characterised using thermal analysis, infrared spectroscopy, and X-ray diffraction. Environmental, technological and cost advantages will make the present process feasible for the manufacture of advanced zirconia-based ceramics.

## Introduction

Zirconia-based ceramics have earned much attention in both the scientific and technological communities due to their superior properties such as: excellent refractance and chemical resistance, good mechanical strength, high fracture toughness and hardness, large ionic conductivity, low thermal conductivity at high temperature, and good thermal stability and resistance to thermal shock. These properties give them great potential for structural and functional applications such as: advanced structural transformation-toughened ceramics for high wear environments *e.g.* engine and machine components and cutting and abrasive tools; piezoelectric and dielectric ceramics; sensors/probes for oxygen transport and detection; solid electrolytes for solid oxide fuel cells and high-temperature water-vapor electrolysis cells; catalysts for automotive exhaust cleaning and the partial oxidation of hydrocarbons; pigments; mixed-conductors exhibiting both oxygen ion and electronic conductivity for oxygen separation membranes and electro-catalysts; thermal barrier coatings; optical coatings; and a buffer layer between superconducting film and silicon substrates.

As such, there has been a growing interest in the preparation of zirconia and zirconia-based ceramic powders with the required characteristics of size, purity, uniformity, crystallinity *etc.* Various physical and chemical preparation routes to the powders have been reported in the literature.[1–10] Particular emphasis has been placed upon co-precipitation, sol–gel, hydrothermal processing, and polymerized complex processes. However, difficulties with most of these techniques, mainly involving cost and environmental issues, preclude their commercial utilization. Therefore, practical methods are still needed for the synthesis of high-quality zirconia powders with the required characteristics.

This study resulted from our efforts to treat effluent from an acrylic acid plant. The effluent contained low molecular weight carboxylic acids (acrylic and acetic acids) which show strong resistance to biological and chemical oxidation, and hence exhibited very high chemical oxygen demand and total organic carbon levels. Incineration appeared to be the only option for the effluent in order to meet the international legislation on plant discharges. In order to seek an alternative technique to the conventional incineration treatment we have reviewed the existing and potentially applicable processes for the extraction and separation of carboxylic acids, and found that none of the now commercially significant extraction and separation techniques (distillation, solvent extraction, adsorption, ion exchange and membrane processes) may be used to separate acetic acid from acrylic acid with a good combination of selectivity, economy, and environmental friendliness.[11] This study will demonstrate that a precursor of advanced zirconia ceramics as well as practically pure acetic acid can be obtained by the metal–organic precipitation process using zirconium oxychloride to treat the effluent. In addition, this study will show that the polymer precursor route employing carboxylic acids in an aqueous environment may eliminate the need for toxic solvents and an anhydrous atmosphere, as required for the well-known metal alkoxide sol–gel methods used for the preparation of zirconia powders with well-defined particle size, purity, and crystal polymorphology. Furthermore, the present process is the first example of the preparation of pure, nanoscale, partially stabilized zirconia powders using technical-grade zirconium oxychloride and the effluent from an acrylic acid plant.

## Experimental

### Materials

The raw material used in this study was the effluent from the Shanghai Gao-Qiao Petrochemical Plant which manufactures acrylic acid. The effluent contained 0.68 and 3.67 wt% acrylic and acetic acid, respectively. The precipitant used in this work was technical-grade zirconium oxychloride octahydrate

(Jiangsu Dongtai Plant). Zirconyl chloride solution was prepared by dissolving the desired amount of zirconium oxychloride octahydrate in deionized water and then filtering. The composition of the resulting solution was (ppm): Zr $176.28 \times 10^3$, Al $2.08 \times 10^3$, Fe 39.64, Ca 9.96, Si 5.96, Na 7.25, Ti 1.92. Reagent-grade ammonia was obtained from the Shanghai Chemical Reagent Plant and used as received.

### Synthesis

The zirconyl chloride solution (8 ml) was added to the effluent (800 ml) in a beaker and left to stand for a short period, and then concentrated aqueous ammonia was added dropwise to the magnetically-stirred effluent until the pH value of the resulting solution reached a desired value, at which point the solution became turbid. After being peptized by heating the beaker in a water bath or aged for 2 days, the resultant precipitate was filtered, thoroughly washed with deionized water followed by absolute alcohol, and then dried in an oven at 70 °C for one day. The dried precipitate, *i.e.*, xerogel, is a precursor of zirconia ceramics; calcined at 650 °C for 8 h, resulting in an advanced zirconia powder.

### Analyses

Acrylic and acetic acids were analyzed by using a gas chromatograph (Shimadzu C-R6A Chromatopac, Japan) equipped with a thermoconductive detector and a 10% DNP (2,4-dinitrophenylhydrazine) + ShimaliteF column. The carrier gas was He with a total pressure of 500 kPa. The conditions used were as follows: injector 230 °C, column 110 °C, detector 230 °C.

The chemical composition of the calcined powder was confirmed by X-ray fluorescence analysis and/or inductively coupled plasma-atomic emission spectroscopy using an IRIS Advantage/1000 ICP-AES spectrophotometer (Thermo Jarrel Ash Corporation, USA).

The infrared spectra of the xerogel were recorded using a Bruker Equinox 55 spectrophotometer in the 4000–400 cm$^{-1}$ range with a resolution of 4 cm$^{-1}$ over 25 scans. The xerogel was studied as a powder dispersed in a KBr pellet and was examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) with a thermal analyzer (Universal V2.4F TA Instruments, USA). These experiments were conducted up to 1000 °C with a heating rate of 10 °C min$^{-1}$ in air.

The crystallinity of the calcined powder was determined by powder X-ray diffraction (XRD) using a Rigaku diffractometer (Japan) with Cu-Kα radiation. The crystallite size of the powder was determined by the broadening of the X-ray diffraction peaks using the Scherrer relationship for the diffraction peak widths (full width at half-maximum).[1]

Transmission electron microscopy (TEM) was used to estimate the particle size of the powder and observe the morphology and agglomeration state of the powder. TEM observations were performed in an instrument equipped with a tungsten filament operating at 120 kV (Model JEM-1200EX II, JEOL, Japan) and a point-to-point resolution of 5 Å. Powders were dispersed in ethyl alcohol using an ultrasonic treatment. A drop of the resulting suspension was placed on carbon-coated copper grids, and then the the particle dimensions were measured from micrographs taken with the transmission electron microscope.

Particle size distribution analysis was performed for the powder by the dynamic laser scattering technique using a Mastersizer 2000 (Malvern Instruments, UK).

## Results and discussion

The aqueous solution chemistry of zirconium(IV) has proven to be quite complicated due to the hydrolytic behavior of Group IV complexes, even in strongly acidic solutions. When zirconium oxychloride octahydrate is dissolved in water it gives rise to $[Zr_4(OH)_8]^{8+}$. This species goes into the solution phase with water of hydration and forms the basic zirconyl ion, $ZrOOH^+$. Both $[Zr_4(OH)_8]^{8+}$ and $ZrOOH^+$ may react with acetate ion. Acetate can complex zirconium(IV) and displace the hydroxyl groups in the tetranuclear species $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ present in the Zr(IV) acidic aqueous solution, resulting in soluble hydroxoacetatozirconium chlorides.[12,13] On the other hand, most carboxylic acids are weak acids. Carboxylic acids in aqueous solution mainly exist as monomers because the intermolecular hydrogen bonding between acids is destroyed due to their preferential hydrogen bonding with water molecules. They will partially ionize in aqueous solution according to the equilibrium: $HA \Leftrightarrow H^+ + A^-$. The concentrations of dissociated ($A^-$) and undissociated acids (HA) are affected by the concentration of hydrogen ions (or pH). When the basic zirconyl cation $ZrOOH^+$ comes into contact with the acrylate ion in an acidic solution, they combine to form a precipitate, which consists of cross-linked polymer chains bridged by a zirconium ion.[14] It is, therefore, understandable that acrylic acid (AA) can be precipitated in good yields by the present process while most of the acetic acid (ACA) is retained in the effluent (see Fig. 1). The percentage precipitation of acrylic acid with a given concentration of aqueous zirconium oxychloride solution increases with increasing pH. When the pH is around 6.0, the percentage precipitation of acrylic acid can approach 100%. Above this pH the precipitation tails off. On the other hand, the percentage precipitation of acetic acid gradually rises with increasing pH and even at pH 6.0 or higher only about 10% has precipitated. In addition, it should be noted that zirconium hydroxide precipitate can be produced by the hydrolysis of zirconium oxychloride in aqueous solution with an addition of ammonia at *ca.* pH 2, but in the presence of acrylic and acetic acids a basic zirconium carboxylate would result rather than zirconium hydroxide. At higher precipitation pH values ($\sim$6), however, the formation of some zirconium hydroxide appears to be inevitable, resulting in a relatively low percentage precipitation of acrylic acid. These explanations will be shown to be reasonable by studying the structure of the precipitating complex, as evidenced by the following infrared results.

The mechanism for the formation of zirconia by the present process may be inferred from the thermogravimetric, powder X-ray diffraction, and infrared spectral changes generated
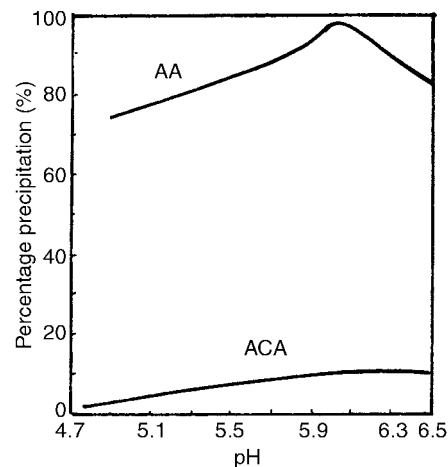


**Fig. 1** Percentage precipitation as a function of pH, for acrylic acid (AA) and acetic acid (ACA) with zirconium oxychloride.
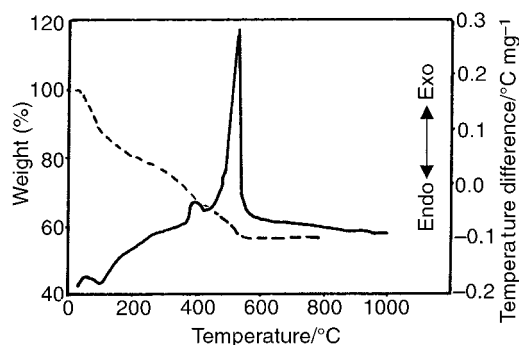
**Fig. 2** DTA and TGA traces of the xerogel. (DTA, solid line; TGA, dashed line).

during the pyrolysis of the xerogel. The DTA and TGA curves for the xerogel are illustrated in Fig. 2. The xerogel is found to decompose to zirconia in three steps, as shown in the DTA curve. There exists an endothermic peak at about 98 °C, which corresponds to the dehydration of the precipitating complex and the loss of physically adsorbed water from the xerogel. The corresponding weight loss obtained from the TGA curve is about 12%. There are two exothermic peaks present in the DTA trace, one centred around 391 °C, and the other centred around 527 °C. The first exothermic peak may be attributed to the decomposition of the precipitating complex (zirconium acrylato and acetato complexes), which gives rise to the formation of cubic zirconia as shown in the powder XRD pattern (Fig. 3a), carbon dioxide, water vapour, carbonate or oxycarbonate groups. At higher temperatures (around 527 °C), the cubic zirconia turns out to be a mixture of cubic and monoclinic phases in which the prevailing phase is cubic as shown in the powder XRD pattern (Fig. 3b), and the carbonate or oxycarbonate groups are decomposed. This decomposition should be responsible for the second exothermic peak. The corresponding weight losses for the two exothermic steps, as estimated from the TGA curve, are about 21 and 8%, respectively, suggesting that most of the precipitating complex should be decomposed in the first exothermic step. In addition, the TGA curve shows that no further weight loss is observed above 527 °C, indicating that the temperature seems to be sufficient for the calcination of the xerogel. It is, however, necessary to heat the zirconia powder to 650 °C to completely eliminate carbon. At 650 °C zirconia is transformed into a mixture of tetragonal and monoclinic phases in which the monoclinic phase is predominant, as shown in the powder XRD pattern (Fig. 3c). The above discussion will be also supported by the infrared spectra recorded for the samples obtained at the heat processing temperatures 70, 391, 527, and 650 °C, as described below.

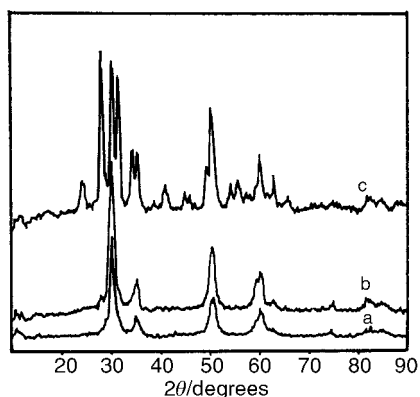Fig. 4(a) shows the infrared spectrum of the xerogel obtained



**Fig. 3** XRD patterns of powders obtained by heating the xerogel at (a) 391, (b) 527, and (c) 650 °C.
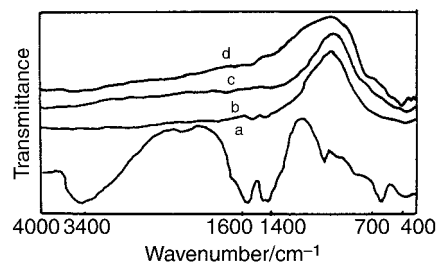


**Fig. 4** IR spectra of the xerogel (a) and powders obtained by heating the xerogel at (b) 391, (c) 527, and (d) 650 °C.

from the effluent by the present process. Some correlations between infrared spectra and structure for zirconium acetate can be found in the literature,[12,15–20] but too little is still known about the infrared spectra of other zirconium acetato complexes and the infrared data for zirconium acrylato complexes are missing from the literature. Therefore, in order to determine the assignments of the bands in the infrared spectrum of the xerogel studied, we have prepared pure zirconium acrylato and acetato complexes and zirconium hydroxide, respectively, and performed the infrared measurements of pure acrylic acid, acetic acid, zirconium acrylato and acetato complexes, and zirconium hydroxide. In addition, these synthesized complexes and the compounds obtained by precipitation from the effluent will be subjected to differential thermal, thermogravimetric and elemental analyses to determine their actual composition, as described in a further publication.

It is widely accepted that the most significant information about the mode of coordination of carboxylic acids can be obtained from the analysis of characteristic frequencies of carboxyl groups. In the infrared spectrum (Fig. 4a) of the xerogel, the broad band centred at 3422 cm$^{-1}$ is due to the OH stretching vibration in the carboxylate and water molecules. There is an indication of unsaturation, *i.e.*, the presence of a shoulder at 1634 cm$^{-1}$ due to C=C stretching vibration in the infrared spectrum of the xerogel, suggesting that the precipitating complex studied may be a zirconium acrylato complex. The broad bands centred at 1565 and 1436 cm$^{-1}$ are ascribed to asymmetric and symmetric stretching vibrations for the carboxylate ion studied, respectively, The frequency separation between the asymmetric and symmetric stretching vibrations of the carboxylate ion is 129 cm$^{-1}$, indicating that the carboxylate ion acts as a bidentate bridging ligand since a purely bridging carboxylate would give rise to larger frequency separation. In addition, the bands at 650 and 446 cm$^{-1}$ may arise from a deformation mode of the carboxylate group and Zr–O bond, respectively. Overall, these characteristic infrared bands indicate that the precipitating complex studied is a basic zirconium carboxylato complex in which a carboxylate ion is directly bonded to the zirconium of the tetramer $[Zr_4(OH)_8]^{8+}$ mainly in a bidentate bridging coordination mode and hence the tetramers are linked together by the carboxylate ions. In addition, it will be shown that, depending on the precipitation pH values, the zirconium complex is a basic zirconium acrylato complex or an acrylato and acetato complex by using the combined data of thermogravimetric, elemental, infrared spectroscopic, small-angle X-ray scattering, and $^{13}$C and $^{91}$Zr nuclear magnetic resonance studies in another paper.

Fig. 4(b, c, and d) presents infrared spectra of the xerogel heated at different temperatures (391, 527, and 650 °C). It is understandable that the intensity of the band at 3422 cm$^{-1}$, due to the OH stretching vibration in the carboxylate and water molecules, decreases dramatically as the temperature is raised. Fig. 4(b) shows that the intensities of the bands at 1634, 1565, and 1436 cm$^{-1}$, which are typical of carboxylate groups, are significantly reduced in intensity as compared to the spectrum

of the starting xerogel (Fig. 4a), suggesting that most of the precipitating complex has been decomposed at 391 °C. This result is in good agreement with that from the thermal analysis. In addition, Fig. 4(b) exhibits a very broad band centred around 460 cm$^{-1}$, which represents cubic zirconia, confirming the result obtained from the XRD studies. In Fig. 4(c), the bands belonging to the carboxylate groups almost completely disappear indicating that the decomposition of the precipitating complex is substantially complete around 527 °C, and some weak bands corresponding to monoclinic zirconia appear in the very broad band centred around 460 cm$^{-1}$, indicating the presence of some monoclinic phase instead of part of a cubic phase in the zirconia obtained at 527 °C. As the temperature is raised to 650 °C (Fig. 4(d)), the bands at 737, 578, 512 and 443 cm$^{-1}$, belonging to monoclinic zirconia, become sharper. This indicates that the monoclinic phase is predominant in the zirconia obtained at higher temperature (650 °C), because the infrared spectrum of monoclinic zirconia is distinguished by an increase in the number and sharpness of the bands, and the band at about 740 cm$^{-1}$ is distinctive for this phase.[1,21] This result is also consistent with the conclusion from XRD and thermal analyses, as discussed in the above section.

The major impurities, except $H_fO_2$, in the zirconia powder prepared by the present process from technical-grade zirconium oxychloride and the effluent of an acrylic acid plant were: $Al_2O_3$ 0.31, CaO 0.11, $Fe_2O_3$ 0.08, $SiO_2$ 0.07, $TiO_2$ 0.03, $Na_2O$ 0.05 wt%. The reason why the high-purity zirconia powder can be prepared by the present process from the technical grade zirconium oxychloride may be that at *ca.* pH 2.0 only the zirconyl salts would react with polyacrylic acid to form a precipitate,[14] and that even if the pH value of the effluent is adjusted with ammonia to *ca.* 5.5, most other multivalent metal ions can only be precipitated, to some extent, due to the formation of soluble metal complexes with acetic acid present in the effluent.

The microstructure of the powder prepared by the present process was examined by TEM, as shown in Fig. 5. It is visualized from the transmission electron micrograph that the near-spheroidal and less-agglomerated powders may be composed of three kinds of microstructural subunits with different sizes: (a) the first are the primary crystallites with a mean diameter of about 13 nm, which is in approximate agreement with the crystallite size (about 9 nm) determined by
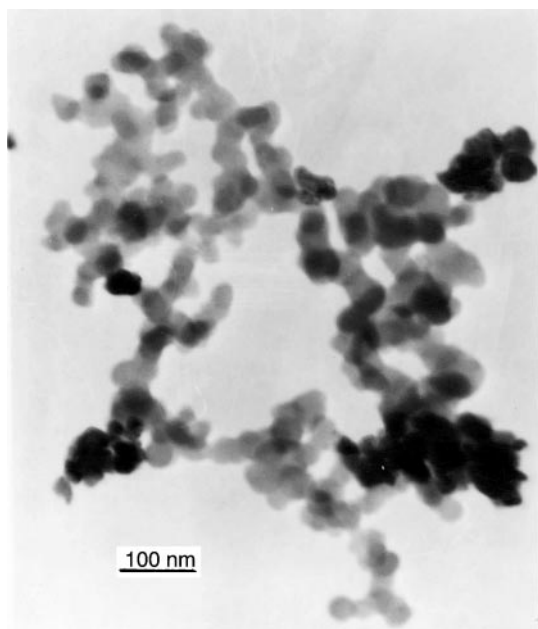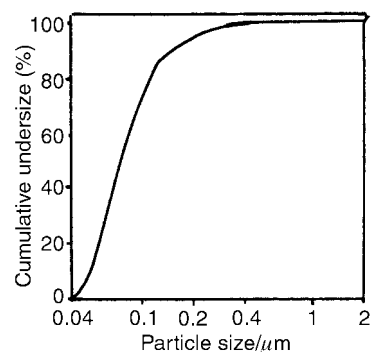


**Fig. 6** A typical particle size distribution of the powder produced by the present process.

X-ray line broadening; (b) the second are formed by aggregates or domains with a narrow size distribution (~50 nm average size) composed of several primary crystallites linked by necks; and (c) the third are agglomerates with irregular shape and size ranging from tens to several hundreds of nanometers, formed by the union of some domains (3 to 6) held together in a chain-like manner by weak attractive forces.

Particle size distribution is undoubtedly the one parameter that, more than any other, influences the powder characteristics, rheology, sinterability and reactivity, and, hence, the apparent density and physical properties of the finished products. It should be pointed out, however, that a crude estimate of the apparent particle size can only be made by conventional measurement methods, *i.e.*, application of the Scherrer equation to the powder X-ray diffraction line-widths, and transmission electron microscopy. Particle size distribution must be obtained by the Stokes' Law sedimentation technique or dynamic laser scattering. It can be found from Fig. 6 that the particle size (D50) of the powder that had been calcined at 650 °C and milled only for 15 min was 80 nm, and the number percentage of the particles below 100 nm and 400 nm were 69% and 99.5%, respectively, indicating that the powder was composed of ultrafine particles with a narrow particle size distribution. Therefore, this study demonstrates that the chemical precipitation process is among the simplest for the rapid synthesis of large amounts of zirconia powders with the same level of quality as those obtained by conventional sol–gel processing techniques. The precipitation process, in contrast to the sol–gel technique, avoids the use of metal alkoxides as precursors which are plagued with problems of higher-cost and more difficult control over stoichiometries and processing environment.

## Conclusions

We have solved a challenging and unique separation problem, *i.e.*, separation of low molecular weight carboxylic acids (acetic acid from acrylic acid) by a metal–organic precipitation process using zirconium oxychloride. In addition, this study demonstrates that both practically pure acetic acid and a precursor of advanced zirconia ceramics can be obtained by the metal–organic precipitation process using zirconium oxychloride at *ca.* pH 6.0 from the effluent of an acrylic acid plant, resulting in near-zero discharge during the production of acrylic acid. The precursor is a basic zirconium carboxylato complex in which a carboxylate ion is directly bonded to the zirconium of tetramer $[Zr_4(OH)_8]^{8+}$ mainly in a bidentate bridging coordination mode and hence the tetramers are linked together by the carboxylate ions.

The thermal decomposition process of the precursor to a partially-stabilized zirconia has been explained on the basis of the combined data of thermal analysis, infrared spectra, and X-ray diffraction measurements. A fully-stabilized cubic zirconia



**Fig. 5** Transmission electron micrograph of the powder prepared by the present process.

may be obtained from the precursor at lower temperature (391 °C). As the temperature is raised to 527 °C, the cubic zirconia turns out to be a mixture of cubic and monoclinic phases in which the prevailing phase is a cubic one. Furthermore, when the temperature is raised to 650 °C, zirconia is transformed into a mixture of tetragonal and monoclinic phases, in which the monoclinic phase is predominant.

## Acknowledgements

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