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Articles

Preparation of Multicomponent Powders by Alkoxide Hydrolysis. 1. Chemical Processing

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A series of chemical processes, based on alkoxide hydrolysis, has been developed as a general technique for preparing multicomponent, ceramic-precursor powders. The basic approach for preparing such powders (where coprecipitation, cohydrolysis, or sol−gel preparation involving all components is difficult, or impossible) involves (i) preparation of an initial homogeneous hydrolysate containing as many components as possible and (ii) sorption of any additional components, as soluble species or as sols, onto the surface of the hydrolysate. This hydrolysate/sorption technique has been used to produce powders with such varied compositions as titanate-based dielectrics, lead zirconate titanate, lead lanthanum zirconate titanate, mullite, zirconia-based ceramics, etc. An example of this approach is provided by the preparation of the multicomponent titanate ceramic, Synroc, which has been produced on a 100 kg scale. The method involves the base-catalyzed hydrolysis of a concentrated solution of titanium, zirconium, and aluminum alkoxides in ethanol, and subsequent sorption of barium and calcium species under alkaline conditions. The initial formation and hydrolysis of Ti/Zr/Al alkoxide complexes was examined semiquantitatively by FT-IR spectroscopy and partial charge model analysis of the charge distribution in the metal complexes and hydrolysate particles. These calculations also identified the principal sites at which propagation and particle growth occurred during polymerization of hydrolyzed alkoxide monomers. In addition, variations in the conductivity of the bulk solution phase were used to characterize reactions occurring at the solid/solution interface during hydrolysis, particle growth, and sorption of alkaline-earth cations. The effects of processing parameters on particle nucleation and selected powder properties are discussed.

Introduction

During the past decade, there has been considerable interest in the preparation of multicomponent powders with carefully controlled morphology and composition.[1] A limitation of many reported methods for preparing multicomponent powders is the use of relatively expensive precursors, especially for nonhydrolyzable cations such as alkali or alkaline-earth species. Such laboratory-scale techniques, while yielding powders with desirable properties, are often unsuitable for processing on an industrial scale.

A series of chemical processes, based on alkoxide hydrolysis, has been developed at ANSTO for preparing multicomponent ceramic precursor powders. The basic approach for preparing such powders (where coprecipitation, cohydrolysis or sol−gel preparation involving all components is difficult, or impossible) involves (i) forming a hydrolysate, precipitate or sol containing as many of the required components as possible and (ii) incorporating any additional components either as free ionic species, or, preferably, by sorption onto the surface of the hydrated oxides produced in step i. A wide variety of multicomponent powders can be readily produced via step i, using either inorganic salts or metal−organic precursors.[1] However, more complex systems, particularly those containing nonhydrolyzable cations, frequently require the sequential application of both steps i and ii. An example of this latter approach is provided by the preparation of the multicomponent, multiphase, titanate ceramic, Synroc, designed to immobilize high-level waste (HLW) produced by the nuclear industry.[2,3] The Synroc precursor powder contains TiO_2, ZrO_2, Al_2O_3, BaO, and CaO in mass abundances of 71.5, 6.9, 5.3, 5.4, and 10.9%, respectively. It has been produced on a 100 kg scale[4] by the base-catalyzed hydrolysis of a concentrated solution of titanium, zirconium, and aluminum alkoxides and subsequent sorption of barium and calcium cations under alkaline conditions. Such techniques yield reactive and readily densifiable pow-

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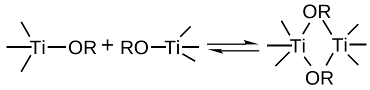
ders,[4] with a high degree of purity and chemical homogeneity, and surface areas in excess of 400 $m^2\ g^{-1}$.

The hydrolytic chemistry of titanium, zirconium and aluminum alkoxides has been investigated extensively.[5–8] Those studies revealed that the rates of alkoxide hydrolysis and the physical properties of the resulting hydrolysate depend upon both the nature of the alkoxy group[6,9] and processing parameters such as pH.[5] An important feature of the chemistry of transition-metal alkoxides is the formation of oligomers, in which the metal ion increases its coordination number by using vacant orbitals to accept oxygen lone electron pairs. This may occur either by alcolation (in a nonpolar solvent):



(1)

or by solvation in polar solvents:

$$2[Ti_3(OEt)_{12}] + 6EtOH \rightleftharpoons 3[Ti_2(OEt)_8\cdot 2EtOH] \quad (2)$$

where OEt and EtOH refer to ethoxy and ethanol, respectively.

The early studies by Yoldas[10] and Bradley and coworkers[6,11,12] emphasised the importance of these processes during hydrolysis and condensation. Livage et al.[5] have also stressed the role of pH in controlling hydrolysis, particle growth, and particle morphology and showed that acid-catalyzed hydrolysis of titanium alkoxides yielded linear, polymeric species with minimal cross-linking, while base-catalyzed hydrolysis produced strongly cross-linked products.

This paper reviews those aspects of the Synroc process chemistry which are generally applicable to the production of multicomponent powders, with controlled properties, from alkoxides. The chemical reactions which occur are discussed, including the formation of alkoxide complexes in ethanol, their hydrolysis, and the subsequent sorption of barium and calcium cations under controlled conditions. The relationship between processing parameters and the properties of the resulting powders is also elucidated.

Experimental Section

Powder Preparation. A flowchart summarizing the processing steps used to produce Synroc powder is shown in Figure 1. Appropriate quantities of tetraisopropyltitanate (TPT), tetrabutylzirconate (TBZ), and aluminum *sec*-butoxide (ASB) were dissolved in an equal volume of anhydrous ethanol. The mixed-alkoxide solution was hydrolyzed at "ambient temperatures" by an excess quantity of water (approximately 24 mol of water/mol of alkoxide) containing dissolved barium hydroxide and finely dispersed calcium hydroxide. A high-shear dispersion mixer, operating at 1500 revolutions/min, was used to ensure intimate mixing during hydrolysis. Component additions were completed during a 60 min interval and the resulting Synroc slurry was agitated for an additional 30 min to promote "equilibration" of the hydrolysate.

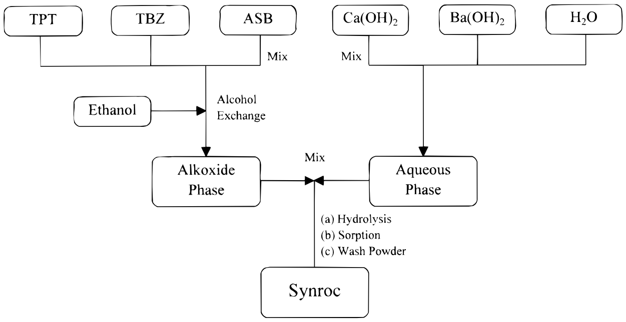


Figure 1. Synroc precursor process chemistry (TPT = tetraisopropyltitanate; TBZ = tetrabutylzirconcate; ASB = aluminum *sec*-butoxide).

Two mixing sequences have been examined in detail:

(a) Water-into-Alkoxide (W→A). The alkoxide solution was vigorously agitated, and the aqueous phase injected into the mixing head, where intimate mixing and hydrolysis occurred. During processing, the temperature of the slurry often exceeded 330 K, as a consequence of the exothermic nature of the hydrolytic reactions. Samples produced by this route are identified as $S_{W\rightarrow A}$ in subsequent discussion.

(b) Alkoxide-into-Water (A→W). In this reverse process, the aqueous phase was agitated, and the alkoxide phase injected. Samples produced by this route are referred to as $S_{A\rightarrow W}$.

The precursor powder was processed in batch sizes of up to 100 kg on an oxide basis.[4] Samples were taken at predetermined intervals during processing and were centrifuged for approximately 2 min to separate the solid and supernatant phases.

Characterization of Powders, Slurries, and Supernatant Solutions. The conductivity of centrifuged supernatant solutions was measured using a Radiometer CDM-83 conductivity meter, equipped with a shielded electrode having a nominal cell constant of 1 cm^{-1}. The electrode was calibrated using standard NaCl solutions. Attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectra (Bio-Rad FTS-40 spectrometer, Harrick single-pass ATR accessory, with ZnSe crystal) of selected slurries were obtained using a bandpass of 2 cm^{-1}. Subband analyses of the spectra were undertaken using software applied by Bio-Rad. The electrokinetic parameters of the slurries (Matec MBS-8000) were also measured. The specific surface area, pore surface area, pore volume (Micromeritics ASAP 2400), particle size (Malvern Mastersizer and Autosizer IIC), scanning electron micrographs (JEOL JXA-840), and X-ray diffraction (XRD) patterns (Siemens Kristalloflex D500) of selected dried powders were also obtained. Simultaneous thermogravimetric and differential thermal analysis (TGA/DTA) data (Setaram TAG 24) were obtained using a heating rate of 10 K min^{-1} in air.

The relative stability of surface species in aged $S_{W\rightarrow A}$ slurries was investigated by leaching with ethylenediaminetetraacetic acid (EDTA) solutions. The resulting supernatant liquids were filtered through 0.45 μm membranes and subsequently analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Results

The ATR FT-IR spectra of TPT/EtOH mixtures containing varying quantities of EtOH are given in Figure 2 (the relative quantities of EtOH and TPT used in the mixtures are summarized in Table 1). As expected, the spectra showed that the addition of EtOH to TPT results in the formation of a mixed alkoxide $Ti(^{i}PrO)_{4-x}(OEt)_x$.

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Table 1. Calculated Composition of Mixed Alkoxide Complexes Formed in the System TPT/EtOH

EtOH:TPT mole ratio	calcd [OEt]:TPT mole ratio	calcd free EtOH:TPT mole ratio
0.0	0.0	0.0
1.1	1.4	−0.3
1.8	1.7	0.1
2.7	2.6	0.1
4.1	3.2	0.9
5.3	3.5	1.8

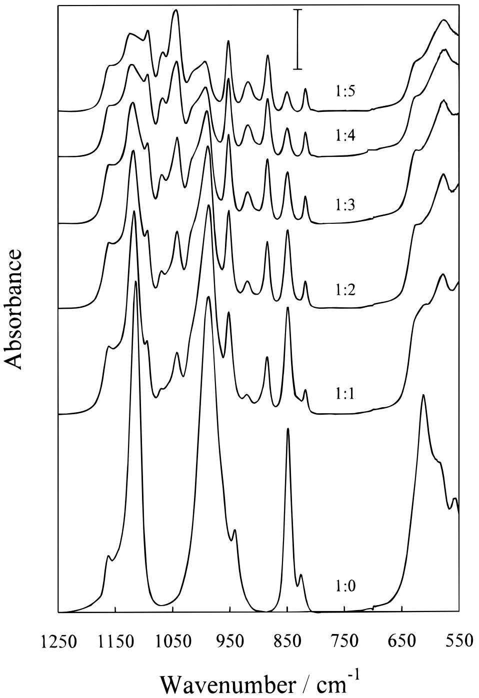

Figure 2. ATR FT-IR spectra of TPT/EtOH mixtures as a function of TPT:EtOH mole ratio (bar = 0.2 absorbance units; exact TPT:EtOH mole ratios given in Table 1).

Complexation was also observed after the addition of ASB to TPT (Figure 3).

Typical variations in the conductivities of centrifuged supernatant liquors obtained during W→A and A→W processing are presented in Figure 4. The conductivity of $S_{W\rightarrow A}$ slurries remained below 15 μS cm^{-1} at all times during processing, reflecting essentially quantitative sorption of alkaline-earth cations onto the surface of the Ti/Zr/Al hydrolysate. In contrast, the conductivity of $S_{A\rightarrow W}$ slurries decreased rapidly from an initial value exceeding 2×10^4 to <20 μS cm^{-1} after 30 min of processing. This result indicates that nearly all alkaline-earth cations initially present were sorbed on the hydrolysate produced during the first 30 min of processing. However, only 50% of the Ti/Zr/Al hydrolysate is produced during this interval, indicating that hydrolysate produced during subsequent processing will be deficient in alkaline-earth species, unless redistribution of the sorbed species occurs.

The relative quantities of Ba(II), Ca(II), and Al(III) species leached from fully processed $S_{W\rightarrow A}$ slurries during treatment with EDTA are illustrated in Figure 5. Ca(II) species appear to be readily leached from the solid phase, while Ba(II) and Al(III) species are somewhat more resistant to leaching.

Selected physical properties of dried $S_{W\rightarrow A}$ and $S_{A\rightarrow W}$ powders are summarized in Table 2.

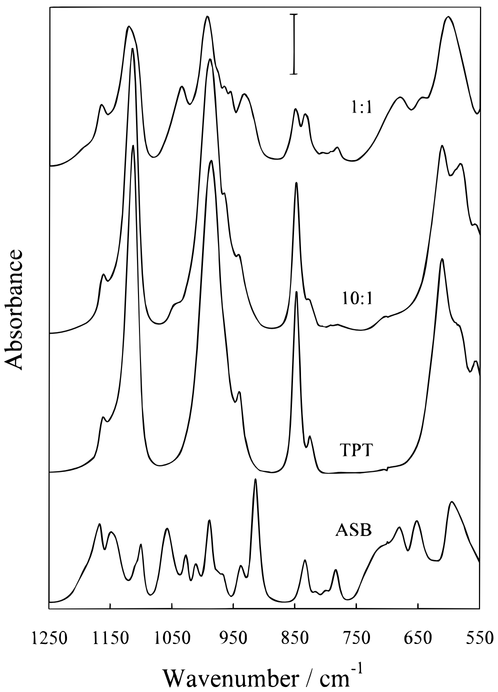

Figure 3. ATR FT-IR spectra of TPT/ASB mixtures as a function of TPT:ASB mole ratio (bar = 0.2 absorbance units).

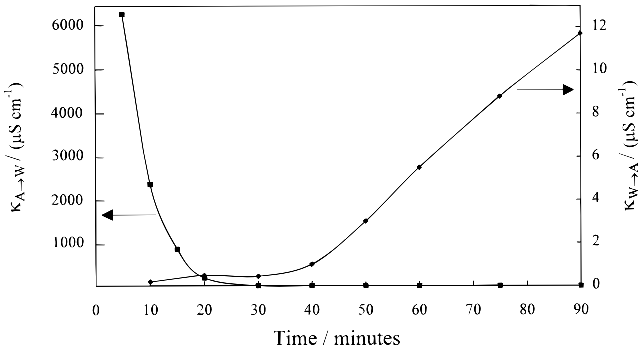

Figure 4. Typical supernatant conductivity as a function of processing time during W→A (■) and A→W (♦) processing.

Discussion

The preparation of Synroc powders involves three distinct chemical reactions:[13]

(a) Formation of a TPT/TBZ/ASB/EtOH complex during mixing of the alkoxides in ethanol.

(b) Hydrolysis of the TPT/TBZ/ASB/EtOH complex, and associated formation of the bulk Ti/Zr/Al hydrolysate and M−OH, [M−O]$^-$, and [M−OH$_2$]$^+$ surface sites (M = Ti, Zr, and/or Al).

(c) Subsequent sorption of alkaline-earth cations onto the negatively charged hydrolysate, leading to the formation of surface sites composed of coordinated Ba^{2+} and Ca^{2+} cations.

Although the properties of titanium, zirconium, and aluminum alkoxides have been investigated in detail,[5] the speciation and hydrolytic chemistry of these compounds may be significantly different when they are mixed together in a polar solvent, such as ethanol.

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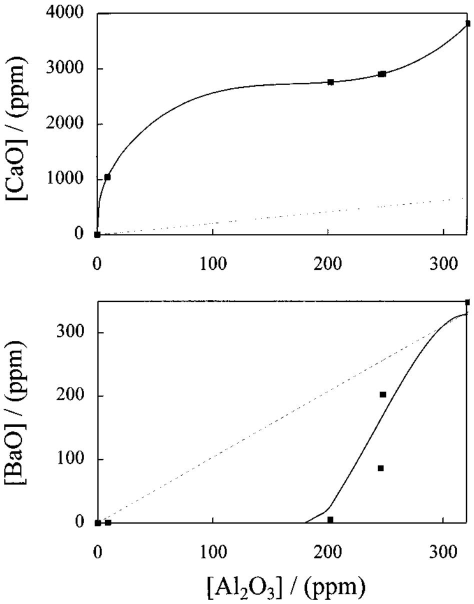

Figure 5. Quantities of Ca(II) and Ba(II) (expressed as parts per million (ppm) of BaO and CaO, respectively) leached from Synroc precursor powders as a function of leached Al(III) (ppm of Al_2O_3), during treatment with EDTA. The dashed lines represent the relative amounts of the respective oxides present in unleached slurries.

Table 2. Physical Properties of Synroc Powders Prepared by W→A and A→W Processing

property	$S_{W \to A}$	$S_{A \to W}$
median particle size (μm) (light scattering)	5−15	10
powder density (g cm^{-3})	3.3 ± 0.2	2.9
IEP (pH)	9.1 ± 0.1	8.15 ± 0.05
tap density (g cm^{-3})	1.4 ± 0.1	0.8 ± 0.1
pore volume (cm^3 g^{-1})	0.2−0.3	0.63−0.64
surface area (m^2 g^{-1})	400−450	430−450
particle morphology (SEM)	raspberry structure	acicular, spherical

Henry[14] and Livage et al.[5] have described a semiquantitative method for examining reactions occurring during preparation of complex systems, such as TPT/TBZ/ASB/EtOH, in which the partial charges of the various functional groups are calculated from the electronegativities of the constituent atoms. Briefly, the electronegativity of an atom changes linearly with its charge:

$$\chi_i = \chi_i^0 + \eta_i \delta_i \tag{3}$$

where χ^0 is the electronegativity of the neutral atom (using Pauling's scale), and η_i is given by

$$\eta_i = k\sqrt{\chi_i^0} \tag{4}$$

where $k = 1.36$ for electronegativities expressed using Pauling's scale. Charge transfer within a molecular system containing n atoms ceases when the electronegativities of the constituent atoms become equivalent to the mean electronegativity $\bar{\chi}$:

$$\bar{\chi} = \frac{\sum_{i=1}^{n}(p_i\sqrt{\chi_i^0}) + kz}{\sum_{i=1}^{n}(p_i/\sqrt{\chi_i^0})} \tag{5}$$

where p_i refers to the stoichiometry of the ith atom in the complex and z is the net charge of the complex. The partial charge, δ_i, is then given by

$$\delta_i = (\bar{\chi} - \chi_i^0)/(k\sqrt{\chi_i^0}) \tag{6}$$

The effectiveness of the partial charge model (PCM) in predicting speciation in inorganic and organometallic systems has been clearly demonstrated,[5,14] despite the approximations involved (e.g., neglect of oligomerization in complex alkoxide systems, etc.).

The electronegativity constants used in the present work were taken from the data of Allred[15] and Rochow.[16] The values reported for χ_C^0, χ_O^0, and χ_H^0 were very similar, and mean values were used in the present calculations. In contrast, the values reported for Al^{3+} were substantially different (1.61[15] and 1.47[16]). The former value was used in this study since it accounted qualitatively for all experimental observations, whereas the latter value gave anomalous results in some instances. The values for the electronegativities of Ti(IV) and Zr(IV) were taken from Allred.[15]

The application of PCM theory to those aspects of the process chemistry that are common to both W→A and A→W processing (e.g., speciation of alkoxide solutions, polymerization reactions, and formation of the ultimate crystallites from which powder agglomerates are composed) is discussed. The major differences in these process chemistries and their influence on powder properties are also discussed.

Complex Formation in Solutions. *Alcoholysis Reactions.* In the preparation of multicomponent powders from alkoxides, it is generally desirable that all the component alkoxides are based on the same alcohol, to ensure that cohydrolysis occurs "simultaneously". In the laboratory, this is possible since they can be synthesized on a small scale. However, it may not be economically feasible when processing on a large scale, since many alkoxides are not produced on an industrial scale. In such cases, it may be possible to dissolve the alkoxides in a large excess of a common solvent alcohol, leading to alcohol exchange and the formation of complexes with the solvent alcohol, which subsequently promotes cohydrolysis. Studies of the speciation of titanium and zirconium alkoxides in EtOH have shown that TPT and TBZ readily react with EtOH molecules to form mixed alkoxides.[17,18]

Addition of EtOH to pure TPT or to mixtures of TPT, TBZ, and ASB leads to an increase in the temperature of the mixture of up to 30 °C above ambient. This suggests that dissolution of the alkoxides in EtOH is accompanied by an alcoholysis reaction. Alcoholysis involves nucleophilic attack of the metal site in an

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(18) Reference 6, pp 27−33.

Table 3. Partial Charge (δ) on (EtOH) and (^{i}PrOH) Species and Predicted Alcoholysis Products, following Addition of 1 mol of EtOH to $\mathrm{Ti}(^i\mathrm{OPr})_{4-x}(\mathrm{OEt})_x$

alkoxide	δ-(^{i}*PrOH*)	δ-(EtOH)	predicted products
$\mathrm{Ti}(^i\mathrm{OPr})_4$	−0.04	−0.12	$[\mathrm{Ti}(^i\mathrm{OPr})_3(\mathrm{OEt})]\cdot[^i\mathrm{PrOH}]$
$\mathrm{Ti}(^i\mathrm{OPr})_3(\mathrm{OEt})$	−0.02	−0.11	$[\mathrm{Ti}(^i\mathrm{OPr})_2(\mathrm{OEt})_2]\cdot 2[^i\mathrm{PrOH}]$
$\mathrm{Ti}(^i\mathrm{OPr})_2(\mathrm{OEt})_2$	0.00	−0.09	$[\mathrm{Ti}(^i\mathrm{OPr})(\mathrm{OEt})_3]\cdot n[^i\mathrm{PrOH}]$, $^i\mathrm{PrOH}$
$\mathrm{Ti}(^i\mathrm{OPr})(\mathrm{OEt})_3$	0.02	−0.07	$[\mathrm{Ti}(\mathrm{OEt})_4]\cdot n[^i\mathrm{PrOH}]$, $^i\mathrm{PrOH}$

alkoxide molecule by a discrete alcohol molecule:[18]

$$\mathrm{M{-}(OR)}_n + \mathrm{R'{-}OH} \rightleftharpoons [\mathrm{M{-}(OR)}_n(\mathrm{OR'})\mathrm{H}]^* \quad (7)$$

The initial step results in the formation of a transition state (depicted by an asterisk) from which an alcohol molecule may be expelled. Four potential terminating steps are (neglecting oligomerization processes)

$$[\mathrm{M(OR)}_n(\mathrm{OR'})\mathrm{H}]^* \rightarrow \mathrm{M(OR)}_{n-1}(\mathrm{OR'}) + \mathrm{R{-}OH} \quad (7a)$$

$$[\mathrm{M(OR)}_n(\mathrm{OR'})\mathrm{H}]^* \rightarrow \mathrm{M(OR)}_n + \mathrm{R'{-}OH} \quad (7b)$$

$$[\mathrm{M(OR)}_n(\mathrm{OR'})\mathrm{H}]^* \rightarrow [\mathrm{M(OR)}_n][\mathrm{R'{-}OH}] \quad (7c)$$

$$[\mathrm{M(OR)}_n(\mathrm{OR'})\mathrm{H}]^* \rightarrow [\mathrm{M(OR)}_{n-1}(\mathrm{OR'})][\mathrm{R{-}OH}] \quad (7d)$$

In reaction 7a, R−OH is eliminated, yielding a new alkoxide molecule, $\mathrm{M(OR)}_{n-1}(\mathrm{OR'})$, while in reaction 7b, R′−OH is eliminated, and no net change occurs. In contrast, in reactions 7c and 7d, neither alcohol is eliminated, leading to partial solvation of the alkoxide molecule by the alcohol (either R′−OH or R−OH). The most probable terminating reaction can be predicted using PCM theory. In a nucleophilic substitution process (reactions 7a and 7b), the leaving group should bear a net positive charge in the transition-state complex. Conversely, if both R−OH and R′−OH carry a net negative partial charge in the transition-state complex, then both will be poor leaving groups, and neither alcohol will be eliminated (reactions 7c and 7d).

The various chemical species predicted in the TPT/EtOH system during stepwise addition of EtOH, and the associated partial charges residing on 2-propanol (^{i}PrOH) and EtOH, are summarized in Table 3. These calculations predict the following:

(a) Addition of 1 or 2 mol of EtOH to 1 mol of TPT will produce solvated complexes such as $[\mathrm{Ti(O}^i\mathrm{Pr})_4(\mathrm{OEt})\mathrm{H}]$ and $[\mathrm{Ti(O}^i\mathrm{Pr})_4(\mathrm{OEt})_2\mathrm{H}_2]$, respectively. Although δ(EtOH) and δ(^{i}PrOH) are both negative under these conditions (implying that both are poor leaving groups), $\delta(\mathrm{EtOH}) < \delta(^i\mathrm{PrOH})$, suggesting that subsequent alcoholysis will occur to yield $[\mathrm{Ti(O}^i\mathrm{Pr})_3(\mathrm{OEt})]\cdot[^i\mathrm{PrOH}]$ and $[\mathrm{Ti(O}^i\mathrm{Pr})_2(\mathrm{OEt})_2]\cdot 2[^i\mathrm{PrOH}]$.

(b) In contrast, addition of 3 mol of EtOH to 1 mol of TPT yields a transition-state complex in which δ(^{i}PrOH) is positive, resulting in the expulsion of 1 mol of ^{i}PrOH and subsequent formation of a mixed, solvated alkoxide (viz. $\mathrm{Ti}(^i\mathrm{PrO})(\mathrm{OEt})_3$).

(c) Similarly, the stepwise addition of 4 mol of EtOH to 1 mol of TPT should yield $\mathrm{Ti(OEt)}_4$.

Analogous calculations for the TBZ/EtOH and ASB/EtOH systems also predict that the corresponding ethoxides will form when the EtOH-to-alkoxide mole ratio (N_{mr}) exceeds 4 and 3, respectively.

The FT-IR spectra of TPT/EtOH mixtures with N_{mr} values between 1 and 5 (Figure 2) confirm that addition of EtOH to TPT yields a mixed alkoxide, according to the equilibrium:

$$m\mathrm{Ti}(^i\mathrm{PrO})_4 + y\mathrm{EtOH} \rightleftharpoons [\mathrm{Ti}(^i\mathrm{PrO})_{4-x}(\mathrm{OEt})_x]_m + mx{}^i\mathrm{PrOH} + (y - mx)\mathrm{EtOH} \quad (8)$$

where $(y - mx)$ represents the moles of EtOH not consumed by alcohol exchange, and m the degree of oligomerization. Although the PCM calculations suggest that complete alcohol exchange will occur in this system (i.e., if $y \leq 4m$, then $mx = y$), a semiquantitative subband analysis of the FT-IR spectra indicates that the exchange is not complete when $y > 3$. For instance, when $y = 4.12$ and 5.33, the measured values of x are 3.2 and 3.5, respectively (instead of 4). On the basis of these results, it can be concluded that under the conditions used to prepare the Synroc precursor powders, alcohol exchange was >80% but <100% complete.

Formation of TPT/TBZ/ASB/EtOH Complexes. The properties of alkoxides in multicomponent mixtures are often substantially different from those of the neat alkoxides, and the mixing sequence can play an important role in determining solution speciation. For example, it has been found in this study that mixtures of TPT, TBZ, ASB, and EtOH readily form transparent, single-phase solutions, whereas mixtures of ASB and EtOH yield a two-phase system consisting of an immiscible ethoxide and a mixture of EtOH and butanol. Hence, the TPT and TBZ must be added to ASB prior to addition of ethanol, during preparation of Synroc precursor alkoxide solutions.

The speciation of ASB molecules in the TPT/TBZ/ASB/EtOH system may also be predicted using PCM theory. The calculated mean partial charge on the [OEt] species in $\mathrm{AlTi}_n(\mathrm{OEt})_{3+4n}$ and $\mathrm{AlZr}_n(\mathrm{OEt})_{3+4n}$, for varying values of n ($0 \leq n \leq 24$) are shown in Figure 6. Increasing n leads to an increase in the negative partial charge residing on the [OEt] ligands and hence to an increase in their electron-donor strengths. As a consequence, it is anticipated that the stability of Lewis donor−acceptor complexes involving $\mathrm{Al(OEt)}_3$ would be enhanced in the heteronuclear $\mathrm{AlTi}_n(\mathrm{OEt})_{3+4n}$ and $\mathrm{AlZr}_n(\mathrm{OEt})_{3+4n}$ clusters, relative to the homonuclear $[\mathrm{Al(OEt)}_3]_m$ species. Although it is difficult to predict the exact composition of the final heteronuclear Ti/Zr/Al clusters using PCM theory, the data in Figure 6 indicate that the donor strength of the [OEt] group remains nearly constant for $n > 4$, suggesting an upper size limit to the oligomers.

The formation of complexes between TPT and ASB molecules, prior to the addition of EtOH, is also clearly reflected in the FT-IR spectra of TPT/ASB mixtures, for ASB:TPT mole ratios between 0.1 and 1 (Figure 3). The spectra of the mixtures cannot be assigned as simple linear combinations of the pure TPT and ASB spectra, suggesting that new molecular species are produced during mixing:

(a) The 914 cm^{-1} band observed in the spectrum of pure ASB is not evident in the spectra of any of the mixtures, even though the weaker 834 cm^{-1} is detected in the spectra of all TPT/ASB mixtures. Various authors[6,19−21] have assigned bands in the region 900−

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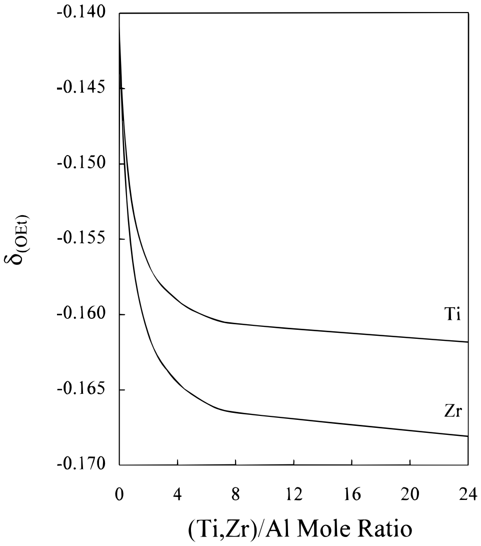


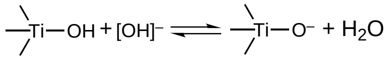
Figure 6. Partial charges residing on [OEt] in the systems $AlTi_n(OEt)_{3+4n}$ and $AlZr_n(OEt)_{3+4n}$ for $0 \leq n \leq 24$.

1000 cm^{-1} in the spectra of oligomeric aluminum alkoxides to ν_{C-O} modes of bridging alkoxy ligands, while the 834 cm^{-1} band appears to be a characteristic feature of the 2-butoxy group.[22] The extinction of the 914 cm^{-1} band in the mixtures (under conditions where the 834 cm^{-1} band is retained) reflects disruption of the oligomeric structure of ASB (molecular complexity = 2.4[6]), leading to the formation of new complexes between ASB and TPT. Related changes are also observed in the ν_{M-O} region 550−700 cm^{-1}, although the complex overlapping profiles in this region cannot be unambiguously assigned to specific molecular species.

(b) An additional band is also evident at 1037−1046 cm^{-1} in the spectra of the mixtures, which has no counterpart in the spectra of either of the single alkoxides. The infrared spectrum of aluminum isopropoxide exhibits a band at 1032−1036 cm^{-1} [21,23−25] assigned to ν_{C-O}. This suggests that the 1037−1046 cm^{-1} band in the TPT/ASB mixtures arises from isopropoxy groups, either covalently bonded to aluminum (as a consequence of alcohol exchange) or coordinated to aluminum sites in the heteronuclear TPT/ASB complex.

The FT-IR spectra of TPT/ASB/EtOH mixtures were also obtained, but the observed spectra could not be assigned unambiguously, due to the complex, overlapping band profiles.

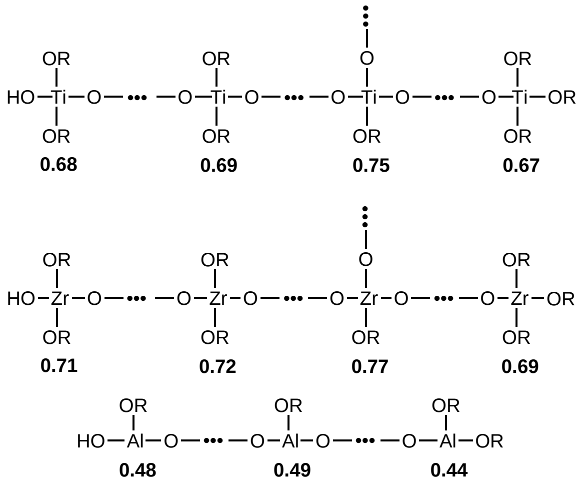
Hydrolysis and Polymerization of TPT/TBZ/ASB/EtOH Complex. Condensation and propagation in base-catalyzed systems, such as those used to prepare Synroc, are generally activated through the formation of strongly nucleophilic species such as [Ti-O]$^-$, [Zr-O]$^-$ and [Al-O]$^-$,[5] e.g.



$$\text{—Ti—OH} + [\text{OH}]^- \rightleftharpoons \text{—Ti—O}^- + H_2O \qquad (9)$$

These reactive, anionic monomers/oligomers would be expected to preferentially bind to the more positively charged metal sites on the growing polymer chain.

Typical Ti, Zr, and Al fragments within the growing Synroc polymers may be represented by



The numbers beneath the site diagrams are the calculated partial charges on the associated metal sites.[5] Under the base-catalyzed conditions used to prepare Synroc powders, the nucleophilic monomers initially formed (e.g., eq 9) will preferentially attach to the more positively charged sites on the growing polymer,[5] and strongly cross-linked species will form.[13] The most active propagation sites appear to be Ti(IV) and Zr(IV) species located within the middle of the propagating polymer chain, promoting cross-linking. The least active growth sites appear to be terminal Zr(IV) and Ti(IV) species and all Al(III) sites. Hence, the polymeric Synroc particles would be expected to be strongly cross-linked, as previously observed for pure Ti(IV) alkoxide systems hydrolyzed under similar conditions.[5]

The relatively low reactivity of the Al(III) sites is of particular interest, since condensation will be effectively blocked at such sites, and they will progressively become concentrated at the surface of the growing colloid. This suggests that a substantial fraction of the Al(III) species may be segregated at the surface of the polymeric particles, rather than being located within the bulk. This conclusion was confirmed by the results of ethylenediamminetetraacetic acid (EDTA) extraction studies (Figure 5), which indicated that a substantial fraction of the Al(III) species in $S_{W\rightarrow A}$ are more readily extracted by complexation with EDTA than Ba(II) surface species. Similarly, acid leaching studies reported by Vance et al. revealed the presence of crystalline $Al(OH)_3$ species in aged Synroc powders, reflecting segregation of Al(III) species during powder production.[26] A similar segregation effect has been reported for zirconium alkoxides modified with β-diketones, where hydrolysis and condensation are essentially "blocked" at the chelated (nonreactive) sites.[27]

Sorption of Cations. Hydrolysis of residual surface alkoxide species on the particles will yield hydroxyl groups, e.g., eq 10. The surface hydroxyls are amphoteric and, depending on the ambient pH, can act either as acids (eq 11) or bases (eq 12). These M−OH, M−O$^-$, and M−OH$_2^+$ surface sites (M = Ti, Zr, and Al) play an important role in the subsequent sorption of soluble

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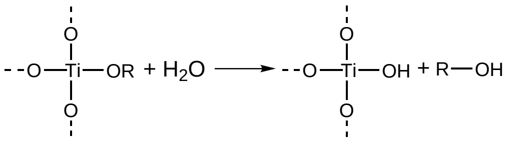
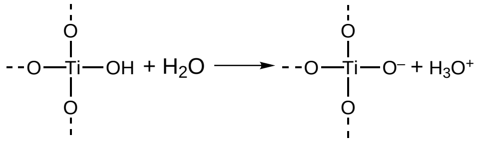
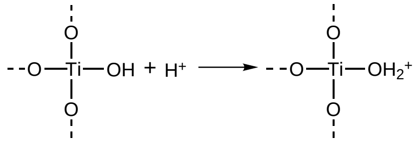


$$\text{--}O-\overset{\overset{\vdots}{O}}{\underset{\underset{\vdots}{O}}{Ti}}-OR + H_2O \longrightarrow \text{--}O-\overset{\overset{\vdots}{O}}{\underset{\underset{\vdots}{O}}{Ti}}-OH + R-OH \qquad (10)$$



$$\text{--}O-\overset{\overset{\vdots}{O}}{\underset{\underset{\vdots}{O}}{Ti}}-OH + H_2O \longrightarrow \text{--}O-\overset{\overset{\vdots}{O}}{\underset{\underset{\vdots}{O}}{Ti}}-O^- + H_3O^+ \qquad (11)$$



$$\text{--}O-\overset{\overset{\vdots}{O}}{\underset{\underset{\vdots}{O}}{Ti}}-OH + H^+ \longrightarrow \text{--}O-\overset{\overset{\vdots}{O}}{\underset{\underset{\vdots}{O}}{Ti}}-OH_2^+ \qquad (12)$$

cations. Under the base-processing conditions used to prepare Synroc powders (see below), the surface of the hydrolysate is always negatively charged, promoting the sorption of the Ba^{2+} and Ca^{2+} cations. A detailed discussion of the interfacial chemistry of the Synroc hydrolysate will be reported in a complementary paper.[28]

Effect of Processing Conditions. The principal ionic species contributing to the conductivity of the supernatant phase during Synroc processing are Ba^{2+} and Ca^{2+}, and their hydrolysis products (i.e., $[BaOH]^+$ and $[CaOH]^+$, respectively). The $[OH]^-$ ion is also expected to contribute to the conductivity during the initial stages of A→W processing, where the pH of the processing medium exceeds 13. Hence, the conductivity reflects the abundance of alkaline-earth species within the supernatant phase during processing; a decrease in the conductivity may be attributed to uptake of cations by the Ti/Zr/Al hydrolysate, while conversely, an increase in the conductivity may arise from desorption of cations.

The conductivity of the centrifuged supernatant solutions obtained at various times during W→A processing generally remains below 15 $\mu S\ cm^{-1}$ (Figure 4), indicating that essentially all alkaline earth cations initially present in the aqueous solution are sorbed on the Ti/Zr/Al hydrolysate. The small increase in conductivity observed during ageing at pH 9–9.5 (i.e., between 60 and 90 min of processing) is probably associated with (i) uptake of CO_2 and subsequent formation of $[CO_3]^{2-}$ or $[HCO_3]^-$ anions and (ii) evaporation of alcohols (e.g., EtOH and ^{i}PrOH) from the slurries, and an associated increase in the mobilities of the free ions.

In contrast, the conductivity of the supernatant phase varied substantially during A→W processing (Figure 4). During the initial 20 min of processing, the conductivity decreased from $>2 \times 10^4$ to approximately 200 $\mu S\ cm^{-1}$, indicating that significant quantities of the ionic species remained within the supernatant phase. Electrokinetic analysis revealed that the $S_{A\to W}$ powders obtained during this interval exhibited a net positive surface,[29] while XRD indicated that the dried samples contained crystalline calcium titanates. After 30 min of processing, the conductivity had decreased to <10 $\mu S\ cm^{-1}$, consistent with nearly complete sorption of all alkaline-earth species initially present. However, only 50% of the Ti/Zr/Al hydrolysate had formed at this time, suggesting that the remaining hydrolysate would be deficient in sorbed alkaline earth species, unless redistribution of these species occurs. $S_{A\to W}$ samples obtained after 40 min of processing did not appear to contain any crystalline species and exhibited a net negative surface charge.

The differing trends in supernatant conductivities observed during W→A and A→W processing reflect significant differences in the compositions of the nucleating particles. The relatively constant supernatant conductivity observed during production of $S_{W\to A}$ suggests that all primary particles have the same composition during nucleation. However, it is evident that the composition of the nucleating particles varies substantially during A→W processing. In particular, the initial primary particles formed during A→W processing contain an excess of alkaline-earth species, while the particles formed during the final stages of processing are deficient in Ba^{2+} and Ca^{2+}. This suggests that particle agglomerates formed during A→W processing may consist of a central region rich in Ba^{2+} and Ca^{2+} species, and an outer skin that is deficient in these species. This expectation has been confirmed by electrokinetic analysis, which indicated that an excess of up to 20% of the alkaline-earth cations in $S_{A\to W}$ slurries may be located within the interior of the agglomerates.[29] Such segregation can lead to inhomogeneities in the composition and distribution of Synroc phases formed during subsequent fabrication operations.

Formation of Bulk Hydrolysate. *Particle Nucleation and Aggregation.* Both W→A and A→W processing yielded very reactive powders with similar specific surface areas, Table 2, suggesting comparable primary particle sizes. The powder density of $S_{A\to W}$ is significantly less than that for $S_{W\to A}$ (2.9 and 3.3 $g\ cm^{-3}$, respectively), indicating greater closed porosity within the $S_{A\to W}$ agglomerates. In contrast, the specific pore volume of $S_{W\to A}$ (0.2–0.3 $cm^3\ g^{-1}$), which reflects open porosity in the agglomerates, is lower than that of $S_{A\to W}$ (0.63–0.64 $cm^3\ g^{-1}$). Hence, $S_{W\to A}$ exhibited the highest tap density.

Two interpretations of these data have been considered:

(i) In the A→W route, the alkoxide solution was added to a large excess of water. Under these conditions, hydrolysis occurs extremely rapidly, with a high rate of nucleation. The high specific pore volume of $S_{A\to W}$ is thus attributed to "colliding growth units" being rapidly locked into place by other primary particles before rearrangement can occur, leading to the formation of very porous agglomerates.[30] In contrast, in the W→A route, when water was added to the alkoxide solution, hydrolysis, polymerization, and nucleation would occur more slowly during processing, allowing the primary particles to arrange themselves into denser agglomerates.[30] Consequently, the powder density should be higher, and the specific pore volume lower, than for powders prepared by the A→W route, as confirmed in Table 2.

(ii) The ionic strength of the A→W reaction medium is substantially higher than that of the W→A medium

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during the first 30 min of processing. Dickinson and co-workers[31] demonstrated the following: (a) Particle agglomeration in high-ionic-strength solutions (diffusion-limited conditions) leads to open, porous structures, with low densities, since the energy barrier to coagulation is lower in high ionic-strength media. (b) Agglomerates formed in low-ionic-strength media (reaction-limited conditions) are more compact, with lower porosity, as the sticking probability is lower in low ionic-strength media.

Both interpretations account for the differences between the structures of $S_{W\rightarrow A}$ and $S_{A\rightarrow W}$ particle agglomerates.

SEM micrographs of $S_{W\rightarrow A}$ powders revealed the presence of raspberry-structure agglomerates (10 μm) which appeared to be composed of spherical particles with an average diameter of approximately 1 μm. No significant variations in agglomerate structure were evident during processing. In addition, no component segregation was observed by energy-dispersive X-ray (EDX) analysis. In contrast, the A→W route produced agglomerates whose morphology varied substantially during processing. Samples obtained after 5 min of processing contained both dense (acicular) and porous (spherical) agglomerates. EDX analysis revealed that the porous particles were titanium-rich, with respect to the bulk, indicating component segregation. These particles were tentatively identified as crystalline calcium titanate, on the basis of XRD and electron diffraction analysis. Samples obtained after 30−70 min of processing contained only acicular agglomerates, and there was no evidence of component segregation or crystallisation in their XRD or electron diffraction patterns. Calcium titanate was only detected in samples obtained during the first 15 min of processing.

Effect of Reactant Concentration. The EtOH content of the alkoxide solutions during processing also has a major influence on the kinetics of hydrolysis, propagation, and nucleation, and on the resulting powder properties:[13]

(i) It changes the alkoxide concentration as follows: (a) during excess-ethanol processing, the decrease in alkoxide concentration accompanying the increased EtOH content decreases the rates of these chemical processes,[13] producing close-packed agglomerates, with lower open porosity; (b) conversely, reducing the EtOH content alters the relative rates of hydrolysis (monomer formation) and condensation (polymer formation),[5] yielding higher open porosity (specific pore volume).

(ii) Second, it alters the relative reactivity of condensation sites on the propagating polymeric particles. A large excess of EtOH leads to a highly cross-linked, dense, “spheroidal” particle, while reduced amounts of EtOH yields a more open, linear structure, with lower skeletal densities.

Applications

Both W→A and A→W processing yielded very reactive powders, with large specific surface areas (Table 2). However, differences in powder properties are evident, permitting some degree of control over the resultant properties. These hydrolysate/sorption techniques have been used at ANSTO to produce multicomponent hydrolysates, powders, and gels with such diverse compositions as Synroc, titanate-based dielectrics, lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT), mullite, zirconia-based ceramics, etc. The hydrolysates can be calcined to form powders with the desired phase assemblage and then fabricated, or they can be used as a precursor and peptized to form sols for subsequent sol−gel processing.[32] The calcined powders have very soft aggregates, which can easily be crushed between fingers, due to processing in large quantities of ethanol. This is important for subsequent fabrication operations.[33]

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