

Amorphous, Monoclinic, and Tetragonal Porous Zirconia Through a **Controlled Self-Sustained Combustion Route**

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Porous, large surface area, metastable zirconias, are of importance to catalytic, electrochemical, biological, and thermal insulation applications. Combustion synthesis is a very commonly used method for producing such zirconias. However, its rapid nature makes control difficult. A simple modification has been made to traditional solution combustion synthesis to address this problem. It involves the addition of starch to yield a starting mixture with a "dough-like" consistency. Just 5 wt% starch is seen to significantly alter the combustion characteristics of the "dough." In particular, it helps to achieve better control over reaction zone temperature that is significantly lower than the one calculated by the adiabatic approximation typically used in self-propagating high-temperature synthesis. The effect of such control is demonstrated by the ability to tune dough composition to yield zirconias with different phase compositions from the relatively elusive "amorphous" to monoclinic (>30 nm grain size) and tetragonal pure zirconia (<30 nm grain size). The nature of this amorphous phase has been investigated using infrared spectroscopy. Starch content also helps tailor porosity in the final product. Zirconias with an average pore size of about 50 μ m and specific surface area as large as 110 m²/g have been obtained.

I. Introduction

 $\mathbf{S}_{\text{ELF-PROPAGATING}}$ high-temperature synthesis (SHS) or combustion synthesis is a well-known method for the preparation of oxide ceramic powders in general and porous zirconias in particular.¹ This method is based on the ability of an exothermic heterogeneous chemical reaction to become self-sustaining and to propagate as a combustion wave through the mixture of reactants. The SHS method has technologically important characteristics like simplicity of the experimental set-up, intrinsic ability of self-purification, and rapidity of synthesis.² However, the rapid self-sustaining nature of the reaction-reaction temperatures, for example, are often estimated by using the adiabatic approximation—also makes it less amenable to control.

We have recently reported the synthesis of macroporous divalent and trivalent metal-oxide foams through a self-sustained combustion method starting from a "dough" containing a natural polymer such as starch.³ The addition of starch is a simple yet effective modification that results in better control over the time-temperature history of the combustion process. The advantage of the modification became more obvious when it was used to synthesize porous zirconia with its grain size-related phase stability.^{4–7} This is demonstrated in the research reported here by the synthesis of pure zirconia in its X-ray amorphous (hereafter referred to as amorphous), tetragonal, and monoclinic forms and with varying surface and pore structures. From a scientific viewpoint, observation of a "pure amorphous zirconia" in particular is interesting as it is a rather elusive phase requiring very small crystallite sizes of the order of 3-4 nm or less.^{6,7} From a technological perspective, the combustion synthesis of amorphous zirconia is important as it provides an alternative route to synthesizing metastable zirconia solid solutions. The production of amorphous and nanocrystalline tetragonal zirconia using a starch-containing gel as the starting material for combustion synthesis has been reported by Tahmasebi and Padyar.⁸ However, detailed correlation between the reason for the formation of these phases, their nature and combustion characteristics was not presented. For instance, flame temperatures were estimated by the adiabatic approximation. It is shown in this paper that while combustion remains selfsustained, the addition of starch changes it enough to render the adiabatic approximation based on completed combustion of starch invalid. In that sense, it is different from combustion routes that have been used to prepare ZrO₂-based ceramics either from solution combustion techniques⁹ or from starting mixtures containing zirconium metal.¹⁰ Also, the exact nature of the combustion-synthesized amorphous zirconia was not further probed by Tahmasebi and Padyar.8

While the method presented here definitely does not yield ordered porous structures, it nevertheless is a simple technique for producing porous zirconia with the desired phase, in potentially large quantities. In combination with good chemical stability and acidic/basic surface adsorption characteristics, such porous zirconias with a large specific surface area are of importance as catalyst and catalyst support for a wide variety of reactions.¹¹ The range of temperatures the porous zirconias are exposed to in these catalytic applications is from 300° to 800°C and the surface area involved is 80–100 m²/g. One particular application of importance is as an anode in solid-oxide fuel cells when combined with Ni to obtain a Ni-YSZ (yttria-stabilized zirconia) cermet. 12

II. Phase Stability in Zirconia-Based Systems

As mentioned before, the effect of starch addition on the combustion process was evaluated using the grain size-related phase stability of zirconia-based systems. Hence, phase stability and its importance from the applications mentioned above is briefly discussed here. Pure zirconia exists in three polymorphic forms—cubic (c), tetragonal (t), and monoclinic (m). The monoclinic phase is the stable form at room temperature, the tetragonal phase above 1170°C and the cubic phase above 2370°C.¹³ Among these phases the high-temperature tetragonal phase is preferred as an active catalyst for organic and petrochemi-cal reactions. For instance, Stichert *et al.*¹⁴ report that for

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Fig.1. Photographs of experimental set-up depicting: (a) electric bunsen with crucible; (b) set-up with thermocouple embedded in the sample; (c) "explosive" flash at the end of combustion in the case where the reaction mixture contains no starch; (d) black carbon ring in case of mixture containing 10 mg starch during active combustion, and (e) completely black sample left behind after combustion in case of the 500 mg starch.

acid-catalyzed n-alkane isomerization reactions, sulfated t-ZrO2 is two to five times more active than sulfated m-ZrO₂. The hightemperature phases of ZrO2 can be stabilized at room temperature by incorporating dopants such as MgO, CaO, Y_2O_3 , and CeO₂ into the crystal lattice.¹³ Alternatively, phase pure *t*-ZrO₂ has also been stabilized at room temperature by preparing nanocrystalline powders below a critical crystallite size of 20-30 nm, known as the Garvie limit, above which it reverts back to the stable monoclinic phase.^{7,15} Stabilization of the tetragonal phase at smaller crystallite sizes or more accurately at larger specific surface areas is due to its smaller specific surface energy. At even larger specific surface areas, an X-ray amorphous phase can be thermodynamically stabilized due to possibly an even lower specific surface enthalpy.^{6,7} It is pointed out though that it is impossible to rule out the presence of small amount of physically or chemically bound water in X-ray or TEM amorphous zirconia. Its observation in general is difficult as zirconia has to be heated very carefully to remove any water present without causing crystallization. The tetragonal to amorphous transition

seems to be energetically favored at crystallite sizes $<4\!-\!5$ nm or equivalent surface area $>\!230$ m²/g.

III. Experimental Details

All the chemicals were used as received without any further purification. Zirconyl nitrate $[ZrO(NO_3)_2 \cdot xH_2O]$ of the purity 99.50% was obtained from Acros Organics (Morris Plains, NJ). Analytical grade urea (99.50% pure) and gravimetric grade starch was procured from Merck Ltd. (Mumbai, India). In a typical experiment, hydrated zirconyl nitrate $[ZrO(NO_3)_2 \cdot 6H_2O]$ and urea were taken in the molar ratio of 1:4.5. According to the principle of propellant chemistry, ¹⁶ the required oxidant to fuel ratio is 1:1.67. However, the ratio of oxidant to fuel is kept higher thereby maintaining the reaction mixture fuelrich. Different amounts of starch {5, 10, 25, 50, 150, 300, 500, and 600 mg per 100 mg (0.31 mmol of ZrO(NO_3)_2 \cdot 6H_2O)} was added to the above mixture and ground until it reached a

dough-like consistency so that it could be easily manipulated into pellets of desired shape. Deionized water, typically < 1 mL/g of the reaction mixture, was added, as required, to get the desired consistency. Combustion of undried and predried pellets showed that this water did not have any significant effect on the reaction characteristics. To perform the combustion reaction a porcelain crucible was placed in an electric Bunsen as shown in Fig. 1(a). It was left to soak for 30 min to remove any possible volatile contaminants and allow temperatures to stabilize. The surface temperature of the crucible bottom was measured using a 0.13 mm diameter, K-type thermocouple to be 400°C. The reaction pellet was then introduced into this preheated crucible. A control experiment was also carried out in the absence of starch. Two types of experiment were performed. In the first type (type-1), the total mass of the reaction pellet was not maintained constant but allowed to increase with the amount of starch. After the combustion process, the reaction product was maintained at the same temperature for 30 min to remove residual carbonaceous material. Unless otherwise mentioned in the text, the data pertain to this type of experiment. In the second type of experiment (type-2), a fixed mass, 175 mg, of the dough was pressed in a steel die to yield cylindrical pellets 6 mm in diameter and 4 mm in height. Following combustion, the pellets were removed immediately without subjecting them to the subsequent 30 min of heat treatment. This set of experiments were designed to factor out possible effects of total mass and morphology of the reaction mixture and the postcombustion heat treatment as in type-1 experiments. In order to estimate combustion zone temperatures, a pellet was formed around the 0.13 mm K-type thermocouple with a 1 s time constant (time to achieve 60% of the value of an instantaneous temperature change) as shown in Fig. 1(b). This assembly was then lowered into the crucible.

The solids were characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential thermal analysis (DTA), surface area measurements, and infrared (IR) spectroscopy. The PXRD patterns of the materials were recorded on a PANalytical X'Pert Pro diffractometer (Almelo, the Netherlands) fitted with secondary graphite monochromator. CuK α radiation ($\lambda = 1.5418$ A) was used. Data were collected at a typical rate of 1°C/min over the 2 θ range of 20°–80°. To identify the tetragonal phase formation wherever required the data were collected at much slower scan rate (0.25°C/min). Crystallite sizes were calculated using the Scherrer equation using peak full widths at half maximum corrected for instrumental broadening. Phase fractions were calculated by using the integrated intensities of the {111} monoclinic and tetragonal peaks.¹⁷ SEM images were obtained using a JEOL JSM 840A microscope (Jeol, Japan). TGA and DTA were carried out using TA Instruments (thermal analyzer) system (New Castle, DE) under continuous air flow with the heating rate of $10^{\circ}/\text{min}$. The specific surface area measurements, average pore diameter, and N₂ adsorption-desorption studies were carried out using a Nova-1000 (Ver. 3.70) instrument (Quantachrome Instruments, Boynton Beach, FL). The samples were degassed at 130°C before measurement. IR spectra were recorded on a Thermo-Nicolet model 400-D FTIR spectrometer (Thermo Scientific, Waltham, MA) (KBr pellet method 4 cm^{-1} resolution).

IV. Results and Discussions

(1) Effect of Dough Composition on Combustion and Phase Stability

The XRD patterns of the ZrO_2 samples obtained in the control experiment (without the addition of starch) and when 5 and 10 mg of starch were added are shown in (Fig. 2). Both type-1 and type-2 experiments have been included. The ZrO_2 obtained in the absence of starch is largely the monoclinic phase (Figs. 2(a) and (b)) with a small percentage of cubic and/or tetragonal phase. The percentage of cubic and/or tetragonal phase increases when 5 mg of starch was used (Fig. 2(c)). In contrast, when the amount of starch used was increased to 10 mg (Figs.



Fig. 2. PXRD patterns of macroporous ZrO_2 obtained when (a) 0 mg (type-2), (b) 0 mg (type-1), (c) 5 mg (type-1), (d) 10 mg (type-1), and (e) 10 mg (type-2) of starch was used in the reaction mixture. The PXRD pattern (d) recorded at slower scan rate in the range $2\theta = 70^{\circ}-80^{\circ}$ is shown as inset. Type-1 and -2 refer to different kinds of synthesis described in the text. *m*, monoclinic; *t*, tetragonal.

2(d) and (e)) pure tetragonal ZrO₂ is obtained. It is difficult to distinguish between cubic and tetragonal phases of nanocrystalline ZrO₂ as the additional peaks that differentiate the tetragonal phase from the cubic phase merge due to peak broadening. However, the (004) and (400) (see inset Fig. 2(d)) reflections corresponding to the tetragonal phase were observed at lower scan rates in the 10 mg starch sample thus confirming its identity. The change in phase composition is accompanied by a reduction in X-ray crystallite size (see Table I) from \geq 30 nm at 0 mg starch to \leq 10 nm at 10 mg. Further increments in starch from 10 to 500 mg, (Fig. 3) and (Table I), have very little effect on phase composition or crystallite size from type-1 experiments. There is a nominal decrease in crystallite size of the tetragonal phase from \sim 9–10 to \sim 7–8 nm. However, a significant

 Table I.
 Crystallite Size and Relative Phase Fractions of Various ZrO2 Samples

Amount of starch used (mg)	Crystallite size (nm)		Phase fractions (%)	
	Tetragonal	Monoclinic	Tetragonal	Monoclinic
0 (type 1)	21	31	29	71
0 (type 2)		41	0	100
5 (type 1)	17	24	59	41
10 (type 1)	9		100	0
10 (type 2)	10		100	0
150 (type 1)	10		100	0
500 (type 1)	8		100	0
500 (type 2)	Amorphous			
600 (type 1)	7		100	0

development at large starch contents such as in the 500 mg sample is the appearance of the amorphous phase in type-2 experiments as seen in Fig. 3 pattern "e."

While the postcombustion heat treatment did not affect the crystallite size of the tetragonal phase and hence the tetragonal to monoclinic transition significantly, it does affect the amorphous to tetragonal transition. As seen from patterns "d" and "e" in Fig. 3, in the sample containing 500 mg starch, type-1 experiments yield tetragonal zirconia whereas type-2 experiments yield amorphous zirconia. The 10 mg starch sample in contrast yielded tetragonal zirconia with a crystallite size of 9–10 nm (see Table I) irrespective of whether it was subjected to postcombustion heat treatment or not. The effect of starch addition on the phases obtained is discussed below by analyzing its effect on the thermal history of the pellet either during or after combustion.

In order to understand the effect of starch addition on the combustion reaction, the manner in which hydrated zirconyl nitrate is converted into dry zirconia during combustion needs to be understood. Hence, pure zirconyl nitrate, pure urea, zirconyl nitrate+urea, zirconyl nitrate +10 mg starch, and zirconyl nitrate+500 mg starch mixtures were subjected to TGA/DTA in air. As can be seen from Fig. 4(a), the TGA data of pure zirconyl nitrate indicate two sharp weight losses at about 100° and 200°C with corresponding endotherms in the DTA data. These are most likely due to loss of physically bound water and nitrate, respectively, leaving behind hydrated zirconia. There is then a period of gradual weight loss till 400°C which is most likely due to removal of chemically bound water. The interesting feature after 400°C is the sharp exothermic peak at 455°C which is not accompanied with any significant weight loss. The only likely source of this peak is an exothermic phase transition such as crystallization. To understand this further and in order to mimic combustion synthesis, i.e. a fast heating rate but in a more controlled fashion, zirconyl nitrate samples were inserted into a furnace set to different temperatures and removed after 1-5 min. As seen from Fig. 5 when inserted at 700°C and removed after 1 min the sample is X-ray amorphous as in Fig. 3, pattern "e." No peaks corresponding to zirconyl nitrate (pattern "a" in Fig. 5) is seen thus implying that it is most likely some form of hydrated amorphous zirconia. The transition to the tetragonal phase is seen only after about 3 min. Similar transitions were observed in all samples heated for 1–5 min from 500° to 800°C. As can also be seen from Fig. 4(b), the main exothermic peak in the DTA data of the mixtures, which is attributed to the combustion process, occurs at about 250°C. The X-ray plus TGA/DTA data unambiguously show that zirconyl nitrate when subjected to combustion synthesis, first gets dehydrated, then calcined to amorphous zirconia, which is then converted to crystalline tetragonal zirconia presumably due to coarsening. The origin of the endothermic peaks in the DTA trace of the mixtures can be easily deduced on comparing with the DTA traces of the pure components of the mixture. The sharp exothermic peak at 450°C in the DTA trace of the 500 mg sample is as discussed later, due to the combustion of residual carbon and not due to the crystallization mentioned above.



Fig. 3. PXRD patterns of macroporous ZrO_2 obtained using (a) 25 mg, (b) 50 mg, (c) 300 mg, (d) 500 mg (type-1), and (e) 500 mg (type-2) of starch in the reaction mixture.

For the purposes of the remaining discussion it will be assumed that the combustion process can be represented by the reactions (1) and (2) below

$$\begin{aligned} &ZrO(NO_3)_2 + 4.5NH_2CONH_2 + 4.25O_2 \\ &\rightarrow ZrO_2 + 5.5N_2 + 4.5CO_2 + 9H_2O \end{aligned} \tag{1}$$

$$C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O$$
 (2)

In simple qualitative terms, the reaction, in the absence of starch and the presence of 10 mg of starch can be described as "explosive" and "smouldering," respectively. A preliminary comparison of the manner in which cylindrical pellets 6 mm in diameter and 4 mm in height, obtained by lightly pressing 175 mg of the dough in a steel die, underwent combustion, illustrates



Fig. 4. (i) TGA and DTA of $ZrO(NO_3)_2 \cdot xH_2O$. The two endotherms at about 115° and 200°C are accompanied with weight losses. In contrast the sharp exotherm at 455°C is not accompanied with any significant weight loss thereby indicating that it is most likely a phase transition such as crystallization; (ii) DTA of (a) $ZrO(NO_3)_2 \cdot xH_2O$, reaction mixtures containing (b) 0 mg, (c) 10 mg and (d) 500 mg starch and (e) urea: the ignition temperature of the reaction mixtures are approximately 200°C when nitrate decomposition starts and large amount of heat is evolved.

this difference. In the absence of starch, the time required for completion of the reaction was about 20 s. The first 17 s involved large scale frothing due to melting of urea and evolution of steam. The evolution of reddish brown fumes and slight discoloration of the frothing mass indicated the beginning of decomposition of nitrate after about 15 s. The mixture then underwent the combustion reaction given by Eq. (1) between the 17th and 20th seconds in an explosive fashion akin to a flare. This last explosive stage is shown in Fig. 1(c). Hence, this process is highly uncon-



Fig.5. PXRD patterns of (a) pure $ZrO(NO_3)_2$, (b) hydrated amorphous ZrO_2 ($ZrO(NO_3)_2$ calcined at700°C for 1 min), and (c) *t*- ZrO_2 ($ZrO(NO_3)_2$ calcined at 700°C for 3 min).

trolled. In contrast, for the 10 mg starch pellet, the reaction was ignited at the bottom of the pellet as soon as it was placed in the crucible within 2 s. A combustion front marked by a black ring due to decomposition of starch could then be seen traveling up the pellet as shown in Fig. 1(d) (reason for the blurry photograph). The fact that combustion is marked by a black ring indicates the heat produced in this case is enough to both decompose starch and initiate ignition of the carbon so formed. In comparison to the 3 s in which the entire mixture flares up in the absence of starch, it took 60 s for the reaction front to go from the bottom to the top of the 4 mm pellet. In the case of the pellet containing 500 mg starch, the beginning of combustion, blackening at the bottom of the pellet, was detected 9 s after insertion into the crucible. It then took the black front 90 s to reach the top of the pellet. The end product is shown in Fig. 1(e).

Maximum temperatures recorded by the embedded *K*-type thermocouple were 400°, 400°, and 390°C for the 0, 10, and 500 mg samples. The recorded temperature is obviously completely incorrect for the 0 mg case. The one measured in the 10 mg case is believed to be an underestimate, while the 390°C temperature recorded in the 500 mg starch case is probably the most reliable of the three readings as discussed in the following sections.

If the process can be considered to be adiabatic in the absence of starch, then a quick calculation using the reaction (1) and data listed in Table II result in an estimated temperature of 2275°C. For doing these calculations, it was assumed that the

	Table II. Data Oseu foi Thermouynan	
Substance	$\Delta H_{ m f}^{\circ}$ (kJ/mol)	$C_{\rm p} (\mathbf{J} \cdot (\mathbf{K} \cdot \mathrm{mol})^{-1})^{18,19}$
$ \frac{CO_2(g)}{H_2O(g)} \\ \frac{H_2O(l)}{H_2O(l)} \\ N_2(g) $	$-393.51^{20} \\ -241.83^{20} \\ -285.83^{20} \\ 0.0^{20}$	$\begin{array}{c} 44.14+9.04\times10^{-3}T-8.58\times10^{5}T^{-2}\\ 30+10.71\times10^{-3}T+0.33\times10^{5}T^{-2}\\ 7+2.6\times10^{-3}T+0.08\times10^{5}T^{-2}\\ 27.20+4.184\times10^{-3}T\end{array}$
$NH_3 (g)$ $NH_2CONH_2 (c)$ $O_2 (g)$ $(C_6H_{10}O_5)_n (c)$ $ZrO_2 (c)$ $ZrO(NO_3)_2 (c)$ $ZrO(NO_3)_2 (c)$	$\begin{array}{r} -45.94^{20} \\ -333.1^{20} \\ 0.0^{20} \\ -1680.17^8 \\ -1100.6^{20} \\ -1346.41^{21} \\ 208.612^{21} \end{array}$	$ \begin{array}{c} 2.726 + 1.161 \times 10^{-1} \\ \hline 29.96 + 4.184 \times 10^{-3} T - 1.67 \times 10^{5} T^{-2} \\ \hline 69.62 + 7.53 \times 10^{-3} T - 14.06 \times 10^{5} T^{-2} \\ \hline \end{array} $
C(s) H ₂ (g)	5000.12	$\begin{array}{c} 17.15 + 4.27 \times 10^{-3} T - 8.79 \times 10^{5} T^{-2} \\ 13.00 + 1.9 \times 10^{-3} T + 1.27 \times 10^{5} T^{-2} \end{array}$

Table II. Data Used for Thermodynamic Calculations

c, crystalline; g, gas; l, liquid; T, absolute temperature.

heat of dehydration of $ZrO(NO_3)_2 \cdot 6H_2O$ is not involved in the combustion process. If included it actually makes reaction (1) an endothermic process. It is assumed that most of this heat is provided by the electric Bunsen which heats up the pellet to >250°C to initiate the reaction by which time most of the chemically bound water is removed as seen from Fig. 3. Furnace experiments showed that it takes 15 min at 1000°C for 9 nm tetragonal powders obtained from combustion synthesis to start transforming to the monoclinic phase following coarsening to beyond 30 nm. Given that this process happens in a few seconds during combustion, the adiabatic estimate of >2000°C in the combustion zone seems reasonable. Thus, in the absence of starch, temperatures are high enough to cause coarsening of tetragonal nuclei beyond the 30 nm limit resulting in the observation of monoclinic zirconia.

In order to estimate combustion zone temperatures in the presence of starch, if the same adiabatic approximation used before were to be used again, then the temperature rise would be given by the equation

$$0.18(1-f)\Delta H_{nitrate} + f\Delta H_{starch} - \Delta H_{vap,water}$$

$$= 0.18(1-f) \left[\int_{298_{I}}^{T} \left[C_{p}^{ZrO_{2}} + 5.5C_{p}^{N_{2}} + 4.5C_{p}^{CO_{2}} \right] dT$$

$$+ 15 \left[\int_{298}^{373} C_{p}^{H_{2}O(I)} dT + \Delta H_{H_{2}O}^{vap} \int_{373}^{T} C_{p}^{H_{2}O(g)} dT \right] \right]$$

$$+ f \left[6 \int_{298}^{T} C_{p}^{CO_{2}} dT + 5 \int_{298}^{373} C_{p}^{H_{2}O(I)} dT + \Delta H_{vap}^{H_{2}O} + \int_{373}^{T} C_{p}^{H_{2}O(g)} dT \right]$$

$$+ \left[\int_{298}^{373} C_{p}^{H_{2}O(I)} dT + \Delta H_{vap}^{H_{2}O} + \int_{373}^{T} C_{p}^{H_{2}O(g)} dT \right]$$

$$(3a)$$

which simplifies to

$$399 \times 10^{3}(1-f) + 1891 \times 10^{3}f$$

= $T^{2}(0.018 + 0.042f) + T(156 + 258f) - 51388$
- $94441f$ (3b)

f is the mole fraction of starch in the reaction mixture and T is the temperature in K. The left side of the above equation is essentially a measure of the heat that would be released in mixtures containing different fractions of starch and the right-hand side is the temperature raise that could be expected given the products as per the reactions (1) and (2) given before. The data used to arrive at Eqs. (3a) and (3b) is listed in Table II. The

adiabatic temperature as function of starch content from Eqs. (3a) and (3b) is plotted in Fig. 6. As seen, starch additions should increase combustion temperature and pure starch would be expected to burn at 3000°C. The experimental results and actual observations point toward the exact opposite or a much lower temperature. Indeed if this were to be true, then the addition of starch should result in a monoclinic product. From type-2 experiments, the addition of 10 mg of starch yields tetragonal zirconia with a 10 nm grain size. Furnace-based experiments to mimic combustion as before indicate that when zirconyl nitrate is directly inserted into a furnace at 900°C it gets converted into crystalline tetragonal zirconia in 60 s, the time required for combustion of the pellet to be completed. Based on this data and actual experimental observation of the combustion process, it is estimated that the temperature of the pellet during combustion on the addition of about 10 mg of starch is about 900°-1000°C, in comparison to 2275°C in the absence of starch. Thus, the addition of just 10 mg (~5 wt%) of starch causes combustion zone temperatures to drop from $>2000^{\circ}$ to about $<1000^{\circ}$ C, instead of raising it as would be expected from adiabatic calculations based on Eqs. (1) and (2). There are three reasons for the observed temperature drop and discrepancy between adiabatically calculated and experimentally



Fig. 6. Plot of the combustion temperature as a function of fraction of starch fraction in the reaction mixture estimated experimentally (using phase composition data as described in the text) as well as calculated assuming adiabatic combustion. The experimentally measured temperature using the embedded thermocouple of 390°C for the reaction mixture containing 500 mg of starch is also shown. The comparison shows that the adiabatic approximation becomes completely invalid when starch is used.

estimated values. Firstly, the fact that the samples containing starch were brownish to black following combustion, indicates that not all carbon is oxidized and thus heat produced would be lower than what is expected from Eq. (2). Secondly, given this observation, it implies that part of the heat from combustion of zirconyl nitrate is used for decomposition of starch and raising the temperature of the decomposition products, namely carbon, hydrogen, and oxygen. A third and probably most important reason is that the combustion of pure starch in air, though selfsustaining, is too slow and cannot be approximated as an adiabatic process. This is illustrated by the following calculation for the 10 mg starch containing sample. Following the reasoning in the two points above, even if it is assumed that starch only decomposes and all hydrogen and carbon so produced remain uncombusted, adiabatic calculations yield a lower bound temperature of 1300°C which is still too high to justify 10 nm tetragonal zirconia. It, thus, makes adiabatic approximation of combustion in samples containing even small amounts of starch, \sim 5 wt%, questionable in the mixtures used herein. Higher starch contents would involve greater deviations. Thus, slow rate of combustion (and therefore greater heat losses), energy consumed in decomposition of starch and incomplete burning of carbon all contribute to a reduction in temperatures when starch is added to the nitrate-urea mixture.

For greater starch contents up to 500 mg, crystallite size data from Table I shows that the temperature of the combustion zone does not change significantly enough to affect coarsening of any tetragonal nuclei formed. However, it does affect the amorphous to tetragonal transition, as type-2 experiments with 500 mg starch yielded amorphous zirconia. Given the TGA/DTA data showing completion of calcination of nitrate at 400°C, the minimum temperature expected is thus 400°C. The fact that the combusted product remains black, see Fig. 1(e), also indicates that temperatures were not high enough to ignite carbon in air. All of these observations are also in fairly good agreement with the measured temperature of 390°C.

What is nevertheless very interesting is that for the 500 mg starch sample, the end product from type-2 experiments is amorphous zirconia. Observation of amorphous zirconia is difficult as any hydrolyzed form of zirconia needs to be heated just enough to remove water without increasing crystallite size to >2-4 nm.⁷ At larger sizes thermodynamics seems to favor the tetragonal phase. Thus, pure amorphous zirconia is in general elusive. While, it cannot be said with complete certainty if whether the amorphous zirconia observed has any bound water or not, it is definitely not the nitrate or tetragonal zirconia as seen from Fig. 4. The IR spectrum of X-ray amorphous zirconia produced by combustion synthesis is shown in Fig. 7(a). The spectrum (a) in Fig. 7 has a broad peak at 3420 cm⁻¹ due to O-H groups and/or absorbed moisture. However, it does not have a peak at 1384 cm^{-1} . This observation suggests that there is no residual nitrate group which is present during the formation of amorphous "zirconia" by combustion. The formula of the compound could then be written as $ZrO_{2-x}(OH)_{2x} \cdot yH_2O$. Spectrum (b) from X-ray nanocrystalline tetragonal zirconia (type-1 experiments) also displays the broad moisture-related peak at 3420 cm^{-1} . The peak at 3420 cm^{-1} is, however, very difficult to eliminate in high surface area materials and hence the most that can be said of the combustion produced amorphous zirconia is that it is at worst a mildly hydrolyzed form of ZrO₂. What the data nevertheless confirms is that there is very little difference between the X-ray tetragonal and X-ray amorphous zirconias. The as-combusted amorphous zirconia is thus "almost" as "ZrO₂" as its crystalline tetragonal counterpart.

Postcombustion soaking in the crucible was found to eventually ignite the carbon left behind over a period of 2-5 min. The exothermic peak observed in Fig. 4(b), trace e, is attributed to the oxidation of carbon. This was verified by the absence of the peak on performing the experiment in nitrogen instead of air. In the process a temperature rise of up to 730°C was recorded by the embedded thermocouple. It must be emphasized that no nitrate containing species could be detected by either XRD or IR



Fig. 7. IR spectra of (a) amorphous ZrO_2 and (b) *t*- ZrO_2 .

spectroscopy in the as combusted mass thereby ruling out this eventual temperature rise to reaction between any leftover nitrate and urea. This temperature rise, as can be seen from Fig. 3(d), is sufficient enough to cause coarsening beyond the limit required for formation of tetragonal zirconia. TGA studies on pellets soaked for 30 min following combustion displayed weight losses of <5% at temperatures $>400^{\circ}$ C implying that such heating is enough to get rid of most of the carbon.

The very fact that we have been able to observe an "amorphous" form of zirconia by combustion synthesis and the fact that it has been reproduced over multiple experiments in a fairly facile fashion is in itself very interesting. Further experiments are underway to better understand the nature of this amorphous zirconia. It opens up the possibility of exploiting SHS further for processing metastable solid solutions through dissolution in amorphous zirconia followed by controlled annealing. The results in the previous paragraph, however, clearly show that any such heat treatment using thermal and/or environmental control, would have to circumvent the problem associated with residual carbon.

(2) Effect of Dough Composition on Porosity

The biggest advantage of the process described in this paper is the ability to produce fine grain zirconia with a large surface area, listed in Table III and a porous structure. The surface areas listed in Table III are from samples subjected to the 30 min posttreatment. The discussion in the previous section showed that the addition of starch had significant effect on the phase composition through its influence on reaction zone temperature and hence grain size, between 0 and 10 mg and relatively little effect thereafter. In this section we show that in contrast starch content between 10 and 500 mg has a significant effect on porosity thus enabling the production of nanocrystalline tetragonal zirconia with qualitatively and quantitatively different surface areas and pore morphologies.

The SEM images of ZrO_2 samples prepared using 0–500 mg of starch are shown in Fig. 8 and the morphology-related data are summarized in Table III. All the samples obtained by the "dough" method used herein have relatively speaking more surface area and pore volume (Table III) than zirconia produced by

 Table III.
 Specific Surface Area, Average Pore Diameter, and Total Pore Volume of Various ZrO2 Samples

Amount of starch used (mg)	Average pore diameter (µm)	Specific surface area (m^2/g)	Total pore volume (cm ³ /g)	Morphology (from SEM)
0	42	38	0.04	Flaky
150	61	26	0.04	Tubular, porous
300	47	110	0.13	Tubes, porous
600	47	78	0.09	Flaky, porous

solution combustion synthesis as would be desirable for catalytic applications. The 150 mg starch sample (Fig. 8(b)) is in particular interesting wherein pores of the order of 100 µm are separated by "walls" which in turn contain another level of porosity in the range of 4-30 µm. The higher magnification images (Fig. 8(c)) of the same sample show the formation of tubes of high aspect ratio on the surface of the porous structure with the average length and the diameter of the tubes being 10-15 and 1 µm, respectively. Such tubular structures were also observed in the porous structure formed up to the addition of 500 mg of starch. While the morphology is affected by the starch content given the nature of the combustion process, there is not much control over tube dimensions. The general trend is that the length and diameter of the tubular structures formed increases with increase in the starch content in the reaction mixture up to 500 mg starch. For larger amounts, e.g. 600 mg of starch, only a flake-like morphology was observed (Fig. 8(d)). Well-defined anisotropic structures were seen only in the 150 mg starch sample.

The formation and evolution of tubular structures on the addition of starch is thought to be due to the method of propagation of the combustion zone, the amount and rate of gases evolved, and the fraction of zirconia forming constituents in the mixture. The following qualitative explanation is proposed. As shown in Fig. 9, it is believed that the combustion from start to finish can be divided into multiple stages. These are similar to the ones discussed before in connection with TGA/DTA data. The length and time scales at which they happen is not clear yet. Step 1 involves drying and leaves behind a cracked structure due to shrinkage on removal of water. Step 2 involves combustion (nitrate decomposition and carbon burn-off) and results in the conversion of the dried dough to zirconia. This step is accompanied by the evolution of gases in addition to water vapor due to drying. This combustion front is preceded

by the drying front and succeeded by the combusted front as shown in step 3 at any point in time. Its propagation through the structure leaves behind the porous combusted product as seen in step 4.

For the formation of anisotropic tubular products, it is essential that the gases produced either due to drying or combustion should be able to leave the system through the existing porous structure (either due to drying as seen in step 1 or previously combusted as in step 3) without causing a local pressure build up. If the rate of combustion is too rapid or if the volume of gases evolved is too large, then local pressure built up will cause fragmentation of the combusted product. As mentioned before in the absence of starch the reaction proceeds almost explosively. It is believed that the absence of any tubular structure when no starch is added is thus due to very high rates of reaction, resulting in local pressure build up and fragmentation of the combusted product. As the starch level increases the reaction proceeds at a lower rate in a manner that can be best described as the movement of a smoldering front like that of a cigarette stick as was also observed by Tahmasebi and Padyar.8 This latter method of combustion is more conducive to the formation of anisotropic tubular products seen, as it allows enough time for gases to escape from the combustion zone. This will result in the anisotropic structure seen in step 4. However, increasing starch levels has two effects. It increases the amount of gas evolved per unit weight of the starting mixture and it also dilutes the concentration of zirconia forming elements in the mixture. It is obvious that as the distribution of zirconia forming elements becomes sparser their ability to form a connected porous product as seen in Fig. 8(b) will diminish. Both, these features could contribute to the absence of tubules at large amounts of starch in excess of 600 mg.

The nonequiaxed morphology of the product implies that the zirconias so formed are not suitable for applications that require



Fig. 8. SEM images of macroporous ZrO₂ prepared using (a) no starch, (b) and (c) 150 mg, and (d) 500 mg of starch in the reaction mixture.



Fig. 9. Stages involved during the combustion process that result in the formation of anisotropic reaction products. With the passage of time the uncombusted mixture first undergoes drying, then combustion to yield the combusted product. UM, uncombusted mixture; DF, drying front; CF, combusted front; CP, combusted product.

good sinterability. Rather, the intended applications are ones in which the large specific surface area can be retained, such as in catalysis. Toward this end, the ability of these zirconias to weather-specific environments would have to be suitably assessed. Retention of the tetragonal phase is expected to be a bigger problem than that of the large surface area. This would then necessitate the need for addition of suitable stabilizers.

V. Summary and Conclusions

Combustion of a dough, obtained by the addition of starch to the starting ingredients of solution combustion synthesis, is considerably different from what is usually considered to be SHS. In particular, while the reaction is self-sustaining, the combustion zone temperatures are much lower from those obtained by adiabatic calculations. In effect, the combustion zone temperature can be controlled by the starch content of the starting dough. This effect of such temperature control in turn helps control the calcination of zirconyl nitrate and coarsening of the zirconia crystallites formed. It thus enables the controlled synthesis of pure zirconia in its monoclinic, tetragonal, and an amorphous form thorough a possible combined effect of crystallite size and hydrolysis level on phase stability. The X-ray amorphous zirconia observed is found to be partly hydrolyzed at worst. By tuning the amount of starch in the starting dough and hence the gas volume formed on combustion, nanocrystalline, (crystallite size between 7 and 10 nm) tetragonal zirconia with a tubular pore structure and surface area between 38 and 110 m^2/g was synthesized.

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