Combustion synthesis: an update

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Abstract

Combustion synthesis has emerged as a facile and economically viable technique for the preparation of advanced ceramics, catalysts and nanomaterials. Recent innovations in the combustion and processing parameters have resulted in a better understanding of combustion phenomena and control of microstructure and property of the products.

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1. Introduction

Combustion synthesis (CS) \cite{1} has emerged as an important technique for the synthesis and processing of advanced ceramics (structural and functional), catalysts, composites, alloys, intermetallics and nanomaterials. In CS, the exothermicity of the redox (reduction–oxidation or electron transfer) chemical reaction is used to produce useful materials \cite{2}. Depending upon the nature of reactants: elements or compounds (solid, liquid or gas); and the exothermicity (adiabatic temperature, $T_{\text{ad}}$), CS is described as: self-propagating high temperature synthesis (SHS); low-temperature combustion synthesis (LCS), solution combustion synthesis (SCS), gel-combustion, sol–gel combustion, emulsion combustion, volume combustion (thermal explosion), etc. Combustion synthesis processes are characterised by high-temperatures, fast heating rates and short reaction times. These features make CS an attractive method for the manufacture of technologically useful materials at lower costs compared to conventional ceramic processes. Some other advantages of CS are:

(i) Use of relatively simple equipment
(ii) Formation of high-purity products
(iii) Stabilization of metastable phases and
(iv) Formation of virtually any size and shape products

The literature on CS is vast and most of the materials prepared and their applications have been summarized in recent publications \cite{2,3,4,5}. The popularity of the method is reflected in the large number of publications on CS appearing in the Materials Science journals and a decade of publication of the \textit{International Journal of Self-propagating High Temperature Synthesis} (Allerton Press, New York).

In our earlier review on CS \cite{1}, we discussed the preparation of a wide range of technologically important materials by SHS, solid state metathesis (SSM), thermite type SHS, gas-phase (flame) synthesis as well as by combustion of redox compounds and mixtures. Currently, we discuss the recent developments in the field with special emphasis on the preparation of ‘Catalysts’ and ‘Nanomaterials’ by solid state combustion (SSC) and solution combustion (SC). Gas phase CS has not been covered.

2. Solid state combustion

In solid state combustion (SSC), initial reactants, intermediates and final products are all in the solid state. Combustion of solid reactants can occur in two modes: (i) linear or self-propagating, high temperature synthesis (SHS) and (ii) bulk or volume combustion synthesis (VCS). In both the cases, the reactants are pressed into a pellet, typically cylindrical in shape. The pellet is then ignited by an external source (e.g. tungsten coil, laser or microwave) either locally (SHS) or uniformly (VCS), which initiates an exothermic reaction. For SHS, the reaction should be highly exothermic ($\Delta H \sim 40 \text{ kcal mol}^{-1}$ or 16 800 J mol$^{-1}$) and the rate of heat generation must be
greater than the heat dissipated; otherwise the reaction will be quenched and will not be self-propagating. The characteristic feature of the SHS mode is that, following local initiation, the hot combustion wave (2000–4000 K) passes through the heterogeneous mixture of reactants yielding the desired condensed product. In VCS (thermoexplosive), the pellet is heated uniformly in a controlled manner until the reaction occurs simultaneously throughout the volume. This mode of synthesis is suitable for weakly exothermic reactions that require activation by preheating or electric field.

Solid state combustion is used in the synthesis of a variety of advanced materials. A general article, ‘Forms from fire’ by Varma [*4] illustrates the simplicity of SSC process for preparing binary refractory materials, intermetallics, and alloys. The materials prepared and their applications are: aluminaides—AlNi (aerospace and turbine material); borides—TiB₂ (abrasives, cutting tool); carbides—SiC, TiC (abrasives and cutting tool); chalcogenides—MoS₂ (high temperature lubricant); hydrides—MgH₂ (hydrogen storage); nitrides—Si,N₄ (ceramic engine parts); oxides—LaₓSrₓCrO₃ (fuel cell interconnect); phosphides—GaP (semiconductor); silicides—MoSi₂ (high temperature heating element) and titanates—TiNi (shape memory alloy). A review article on ‘Combustion synthesis of advanced materials: principles and applications’ [*5], deals with the theory and modeling of SHS reactions based on experimental observations using Time Resolved X-ray Diffraction (TRXRD) and high speed video microscopy. These studies have helped in not only promoting a better understanding of the SSC phenomenon but also in producing tailor-made products e.g. in the formation of titanium silicides (Ti₃Si₄, Ti₅Si₃) of uniform microstructure by carrying out CS with a high density sample [*4,*5].

Recent innovations in the processing of materials involve carrying out SSC in the presence of applied electric and magnetic fields and gravity. Field activated combustion synthesis (FACS) has been employed by Munir and colleagues [6–11] for the synthesis of low enthalpy materials such as metal silicides (V, Cr, W, Nb, Ta), intermetallics (Fe–Al), functionally graded materials (Ti–C–Cu), composites (TiB₂–TiAl₃) and SOFC anode (Ni/YSZ). The main limitations of FACS is that the process cannot be used for reactions that form materials with high conductivity (Nb₃Sn, Nb₃Al) as the current density in the heating zone decreases leading to extinction of the wave.

Similarly, Parkin and his associates have carried out extensive studies on the preparation of soft and hard ferrites by SSC of metal–metal oxide or peroxides in the presence of an external magnetic field [%3,12,13]. It was observed that the velocity of the combustion reaction increases with the application of a magnetic field and the magnetic properties of the products also improve. For example, barium hexaferrite formed in the presence of a magnetic field has greater coercivity and remanence compared to materials prepared in the absence of a field. Similarly, formation of tetragonal CuFe₂O₄ is favoured in the presence of a magnetic field compared to the formation of cubic CuFe₂O₄, which occurs preferentially in the absence of a magnetic field.

Combustion synthesis of TiC and TiC–Al₂O₃–Al, TiB₂–Al₂O₃–Al, ZrB₂–Al₂O₃–Al, Ba,C–Al₂O₃ composites has been studied under microgravity [%5]. These studies show that gravity significantly influences the CS and more uniform microstructured products are formed. This also opens the possibility of production of nanophase materials with high porosity. Varma et al. [14] have investigated the combustion synthesis of Ni–Al-based materials reinforced by TiB₂ particles under both terrestrial and microgravity conditions and they have found that microgravity leads to a decrease in the average TiB₂ size. In addition, an overall decrease in microstructural transformation rates under microgravity was observed.

Solid state combustion has been extensively used to prepare a variety of catalysts e.g. oxynitriles (honeycomb support for noble metals); complex cuprates, LnMCu₃₋ₓ, Ln= Y or La, M=Ca, Ba or Sr (ethylene synthesis); LnCaB₆ (oxidation of methane to ethylene); Fe–Al alloys (ammonia synthesis); modified spinel and Fe–Cr oxides (pyrolysis of diesel fuel) [%3,15]. Other technologically useful materials prepared by SSC are: solid oxide fuel cell materials: Sr and Ga doped LaFeO₃ [16], La₀.ₘ_Sr₀.₁₆_CrO₃ [17], LaₓSrₓCrO₃, FeₓOₓOₙ₋₁, [18], Laₓ, SrₓMnO₃ [19]; the hydrogen storage alloy, MgₓNiH₄ [20] and porous NiTi (biomedical implant material) [21]. Interestingly, a number of nanosize SiC, AlN and Si₃N₄ materials have been prepared by SSC of precursors containing volatile ammonium halides [22] and microwave initiation [23].

3. Solution combustion

The solution combustion (SC) method of preparing oxide materials is a fairly recent development compared to SSC or SHS techniques described above. Today, SC is being used all over the world to prepare oxide materials for a variety of applications. During the short span (15 years) of SC synthesis history, hundreds of papers on SC of oxides have been published, many from the author’s laboratory.

In our previous review [1], we presented a list of oxide materials prepared by rapidly heating aqueous solutions containing stoichiometric amounts of respective metal nitrate (oxidiser) and fuels like urea/hydrazides (carbo hydrazide (CH), oxalyl dihydrazide (ODH), malonic acid dihydrazide (MDH), tetra formal tris azine (TFTA), etc.). A wide range of technologically useful oxides (alumina to zirconia) were prepared with interesting magnetic, dielectric, electrical, mechanical, catalytic, luminescent and optical properties. It was possible to prepare oxide materials with desired composition, structure (spinel, perovskite,
garnets, etc.) by SC. Interestingly, some of the fuels used were found to be specific for a particular class of oxides e.g., urea—for alumina and related oxides; CH—for zirconia and related oxides; ODH—for Fe$_2$O$_3$ and ferrites, TFTA—for TiO$_2$ and related oxides; glycine—for chromium and related oxides, etc.

All these fuels serve two purposes:

(a) They are the source of C and H, which on combustion form CO$_2$ and H$_2$O and liberate heat.

(b) They form complexes with the metal ions facilitating homogeneous mixing of the cations in solution.

The exothermicity ($T_{\text{ad}}$) of the redox reaction varies from 1000 to 1800 K. Depending upon the fuel used, the nature of combustion differs from flaming to non-flaming (smouldering).

The oxide materials prepared and investigated during the review period have been listed in Table 1 along with the fuels used and their applications. Not surprisingly, urea occupies the centre stage, probably due to its ready availability and high exothermicity. Most of the oxides prepared by the urea method are alumina-based e.g. $\alpha$-Al$_2$O$_3$ products [*24]. Another development in alumina synthesis by the urea process is the preparation of nanosize $\alpha$-Al$_2$O$_3$ by microwave initiated SC [25]. The process yields nanosize alumina, since combustion is accompanied by controlled release of gases and dissipation of heat. The ease of doping metal ion in oxides by SC has not only yielded ZTA [26], but has also resulted in the facile synthesis of metal and alloy doped alumina, aluminates [27–29], pigments [30] and phosphors [31,32]. Combustion of aluminium nitrate-urea in the presence of halide salts of Pt, Pd, Ag and Au yielded uniformly dispersed M/Al$_2$O$_3$ composites. These exhibit better catalytic properties towards oxidation of CO and hydrocarbon and

<table>
<thead>
<tr>
<th>Material</th>
<th>Fuel</th>
<th>Particle size</th>
<th>Application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>U</td>
<td>4 $\mu$m</td>
<td>Abrasive</td>
<td>[*24]</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>U</td>
<td>19 nm</td>
<td>Catalyst support</td>
<td>[25]</td>
</tr>
<tr>
<td>Al$_2$O$_3$–ZrO$_2$</td>
<td>U</td>
<td>20–45 nm</td>
<td>Cutting tool</td>
<td>[26]</td>
</tr>
<tr>
<td>MAI$_2$O$_3$ (M=Mn and Zn)</td>
<td>MA+U/CH/ODH/ GLY</td>
<td>15–28 nm</td>
<td>Catalytic support</td>
<td>[27]</td>
</tr>
<tr>
<td>MgAl$_2$O$_4$</td>
<td>U</td>
<td>13–20 nm</td>
<td>Structural material</td>
<td>[28]</td>
</tr>
<tr>
<td>M/MgAl$_2$O$_4$, M=Fe–Co/Ni</td>
<td>U</td>
<td>10 nm</td>
<td>Catalyst</td>
<td>[29]</td>
</tr>
<tr>
<td>Co$^{2+}$/Al$_2$O$_3$</td>
<td>U</td>
<td>0.2–0.3 $\mu$m</td>
<td>Pigment</td>
<td>[30]</td>
</tr>
<tr>
<td>Eu$^{3+}$/Y$_2$O$_3$</td>
<td>U</td>
<td>60–90 nm</td>
<td>Red phosphor</td>
<td>[31]</td>
</tr>
<tr>
<td>Ce$_{1−x}$TbMgAl$<em>2$O$</em>{19}$</td>
<td>CH</td>
<td>10–20 $\mu$m</td>
<td>Green phosphor</td>
<td>[32]</td>
</tr>
<tr>
<td>M/Al$_2$O$_3$, M=Pt, Pd, Ag and Au</td>
<td>U</td>
<td>7–10 nm</td>
<td>Catalyst</td>
<td>[33,34]</td>
</tr>
<tr>
<td>Pd/Al$_2$O$_3$</td>
<td>U</td>
<td>10–18 nm</td>
<td>Catalyst</td>
<td>[35]</td>
</tr>
<tr>
<td>CeO$_2$–ZrO$_2$</td>
<td>ODH</td>
<td>18 nm</td>
<td>Oxygen storage capacitor</td>
<td>[36]</td>
</tr>
<tr>
<td>M/Co$_2$O$_3$, M=Pt, Pd, Ag and Au</td>
<td>ODH</td>
<td>1–2 nm</td>
<td>Catalyst</td>
<td>[38,39]</td>
</tr>
<tr>
<td>Ce$_{1−x}$Pr$_2$O$_3$</td>
<td>CH</td>
<td>4–6 nm</td>
<td>H$_2$–O$_2$ combination catalyst</td>
<td>[39,40]</td>
</tr>
<tr>
<td>Ce$_{1−x}$Pr$_2$O$_3$</td>
<td>CH</td>
<td>3–40 nm</td>
<td>Red pigment</td>
<td>[41]</td>
</tr>
<tr>
<td>Ni-YSZ, (NiCo(Fe/Cu)–YSZ</td>
<td>U</td>
<td>~40 nm</td>
<td>SOFC anode materials</td>
<td>[42,43]</td>
</tr>
<tr>
<td>Ln(Sr)MoO$_3$, M=Fe, Mn and Co</td>
<td>CH/ODH</td>
<td>20–30 nm</td>
<td>SOFC cathode material</td>
<td>[44–48]</td>
</tr>
<tr>
<td>LaCrO$_4$</td>
<td>U</td>
<td>20 nm</td>
<td>Interconnect for SOFC</td>
<td>[49]</td>
</tr>
<tr>
<td>Y$_2$O$_3$–ZrO$_2$–YSZ</td>
<td>CH</td>
<td>59–65 nm</td>
<td>SOFC electrolyte</td>
<td>[50]</td>
</tr>
<tr>
<td>LiCo$<em>{0.5}$Mg$</em>{0.5}$O$_2$</td>
<td>U</td>
<td>5–10 $\mu$m</td>
<td>Cathode material for lithium</td>
<td>[51]</td>
</tr>
<tr>
<td>(M=Ni, Mg, Mn and Zn)</td>
<td></td>
<td></td>
<td>batteries</td>
<td></td>
</tr>
<tr>
<td>MFe$_2$O$_4$/BaFe$_2$O$_4$</td>
<td>ODH</td>
<td>60–100 nm</td>
<td>Magnetic oxides</td>
<td>[52]</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>GLY/CA</td>
<td>18–25 nm</td>
<td>Dielectric material</td>
<td>[53]</td>
</tr>
<tr>
<td>Pb(Zr, Ti)O$_3$</td>
<td>CA</td>
<td>~60 nm</td>
<td>Piezoelectric material</td>
<td>[54]</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>GLY</td>
<td>23 nm</td>
<td>Oxygen sensor</td>
<td>[50]</td>
</tr>
<tr>
<td>ZnO</td>
<td>U</td>
<td>&lt;100 nm</td>
<td>Varistor</td>
<td>[55]</td>
</tr>
<tr>
<td>ZrW$_2$O$_7$</td>
<td>U</td>
<td>38 nm</td>
<td>Negative thermal expansion</td>
<td>[56]</td>
</tr>
<tr>
<td>Eu$^{3+}$/Y$_2$O$_3$</td>
<td>GLY</td>
<td>20–30 nm</td>
<td>Red phosphor</td>
<td>[57]</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>CA</td>
<td>25 nm</td>
<td>Red phosphor</td>
<td>[58]</td>
</tr>
<tr>
<td>In$<em>{2}$Ge$</em>{1−x}$O$_x$</td>
<td>PAA</td>
<td>30–60 nm</td>
<td>Lithium battery</td>
<td>[59]</td>
</tr>
<tr>
<td>In$<em>{2}$Ga$</em>{1−x}$O$_x$</td>
<td>HY</td>
<td>54–160 nm</td>
<td>Optical coating for sensors</td>
<td>[60]</td>
</tr>
</tbody>
</table>

U, urea; CH, carboxylic acid; ODH, oxalylidihydrazide; GLY, glycine; CA, citric acid; PAA, poly acrylic acid; HY, hydrazine; MA, metal acetate.
reduction of NO compared to the conventionally prepared ones [33,34]. Further, it is possible to selectively reduce M^{2+}/Al_2O_3 composites by hydrogen to obtain M or alloy dispersed alumina [35].

Similarly, a variety of ceria and ceria-based oxide materials have been prepared by the SC method using ODH fuel. Some important oxides prepared are: CeO_2–ZrO_2 (oxygen storage capacitor) [36,37], M^{2+}/CeO_2; M=Pt, Pd, Ag, and Au [38] and Ce_{1−x}PtO_2 [39]. Ceria is a well-known catalyst support and Pt/CeO_2 is used in catalytic converters (three-way catalyst TWC) in controlling pollution from car exhausts. Catalytic properties of M^{2+}/CeO_2 were found to be several orders of magnitude better than those reported for the conventionally prepared catalysts. Ionically substituted Pt in CeO_2 (Ce_{1−x}PtO_2) is found to be a particularly good catalyst for H_2–O_2 recombination forming water at room temperature and is being developed as catalyst for valve regulated lead acid (VRLA) batteries with a long life of 15–20 years [40]. Praseodymium doped ceria (Ce_{1−x}PrO_2) prepared by SC is a red ceramic pigment in demand for replacing toxic Cd-sulpho selenide red pigment [41].

Another important application of SC is in the preparation of solid oxide fuel cell (SOFC) materials e.g. M/YSZ (M=Ni, Co (anode) [42,43], LnMO_3 (cathode) [44–48], LaCrO_3 (interconnect) [49] and YSZ (electrolyte) [50]. Table 1 also lists other useful oxide materials prepared by SC such as: cathode material for lithium batteries (LiCo_{0.5}Ni_{0.5}O_2, M=Ni, Mg, Mn and Zn), ferrites (magnetic), dielectric and piezoelectric materials (BaTiO_3, Pb(Zr,Ti)O_3) [51–54], ZnO (varistor) [55] and ZrW_2O_8 (negative thermal expansion material) [56], yttria-based red phosphor [57,58], LiMn_{2}O_4 [59] and In_{0.5}Ga_{0.5}O_3 [60].

Recent research on SC has been directed towards a better understanding of the role of the fuel in controlling the particle size and microstructure of the combustion products. Interestingly, combustion of metal nitrate–glycine–ammonium nitrate redox mixtures [50] or metal acetate–aluminate mixture redox mixtures exhibited non-flaming linear combustion to yield nanosize oxide products [27]. Voluminous zirconia, t-ZrO_2 formed by the combustion of aqueous solution containing a ZrO(NO_3)_2–glycine redox mixture is shown in Fig. 1. Formation of nanosize (≏20 nm) t-ZrO_2 having large surface area (17 m^2/g) has been confirmed by TEM and surface area measurement. Other oxides were prepared using glycine fuel are CeO_2–ZrO_2 and YSZ [50].

In brief, recent investigations on SC have led to the preparation of nanosize materials:

(a) By using the precursors like metal acetates and glycine, one can control combustion and prepare nanosize oxides.
(b) Carcinogenic hydrazine-based hydrazide fuels can be avoided.
(c) Combustion can be initiated by microwave, which yields uniform, narrow size distribution products.

Fig. 1. t-ZrO_2 as formed by the combustion of ZrO(NO_3)_2+Glycine redox mixture.

4. Conclusions

Combustion synthesis appears to meet the demands of Material Science Engineering in tailor making materials with desired composition, structure and property. Surprisingly, by controlling the processing parameters such as microwave initiation, gravity, precursors and additives to redox mixtures, it has been possible to obtain nanosize oxide, carbide and nitride materials and M/oxide composite catalysts using both SSC and SC. The usual processes practiced for the synthesis of nanomaterials are either by the breaking-down (physicists approach) or building-up (chemists approach) methods. Most of these procedures are too involved, need special equipment and expensive raw materials. The combustion method of preparing nanocrystalline materials although it appears to be a breaking down (destructive) process, is in fact, a building-up process as the product nuclei are formed initially and grow.

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* of special interest;
** of outstanding interest.


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