Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 26 (2006) 3365–3372
www.elsevier.com/locate/jeurceramsoc

Influence of combustion aids on suspension combustion synthesis of mullite powders

O. Burgos-Montes, R. Moreno, M.T. Colomer, J.C. Fariñas *

Instituto de Cerámica y Vidrio (CSIC), c/Kelsen n° 5, Cantoblanco E 28049, Madrid, Spain

Received 13 May 2005; received in revised form 3 August 2005; accepted 8 August 2005
Available online 23 September 2005

Abstract

Mullite powders were obtained by suspension combustion synthesis. The reaction was performed in a combustion reactor designed in the laboratory, which presents some advantages over other classical procedures (heating with a hot-plate, a furnace or a microwave oven). Aluminium nitrate, as a source of Al, and either TEOS or a colloidal silica suspension, as a source of Si, were used as reagents. Urea, at either 100 or 200% excess over the stoichiometric ratio, was used as fuel. NH_4NO_3, HNO_3, NH_4Cl and H_2O_2 were compared as combustion aids. Mullite phase with a high crystallinity and a high specific surface area was directly obtained by using aluminium nitrate, colloidal silica suspension, a 100% excess of urea and either NH_4NO_3 or H_2O_2. The selection of a combustion aid determines the characteristics of the as-synthesized powders. In addition to enthalpy predictions the reduction potential is a key parameter for the combustion to occur.

Keywords: Powders-chemical preparation; Suspensions; Mullite; Combustion synthesis

1. Introduction

Mullite and mullite–matrix composites have been extensively used as structural materials due to their excellent high temperature mechanical properties.[1,2] Bulk mullite bodies can be obtained by conventional powder processing routes, but their consolidation into dense compacts requires relatively high sintering temperatures. For this reason, the preparation of mullite powders with fine particle size and higher reactivity is receiving increased attention.[3]

The most popular methods for the production of reactive mullite powders include the use of precursor solutions (e.g. in the sol-gel process) which react to form mullite after densification,[4] coprecipitation from aluminium nitrate enneahydrate and colloidal silica sols,[5] and by heterogeneous nucleation and growth processing.[6]

An attractive route to produce homogeneous, fine and crystalline oxidic ceramics without intermediate thermal treatments is the solution combustion method that has received great attention in the last years.[7] The process is based on the mixing of reactants that oxidize easily, such as nitrates, and an organic fuel, acting as a reducing agent. An external heat supply is needed to promote the ignition of the mixture leading to a self-sustaining and exothermic redox reaction.

As oxidisers, metal nitrates of the desired cation are preferred because they are water-soluble, contain nitrogen, and they usually melt at only few hundred degrees. When the nitrates of the elements of interest are not available, as it happens for Si or Ti, metal-organic compounds are used, such as tetraethylorthosilicate (TEOS) for Si,[8] and titanium isopropoxide for Ti.[9]

As fuels, molecules containing carboxylic and/or amine groups are mainly used, since they are a source of C, N and H, which form CO_2, NO_x and H_2O liberating heat.

Urea (CH_4N_2O) is the most popular fuel because it is commercially available, cheap, produces high temperatures and generates low volume of gases.[7] The following reagents including C, N and H in their composition have been used: glycine ($C_2H_5NO_2$),[10] ammonium acetate ($C_2H_7NO_2$),[11] carbohydrazide (CH_6N_4O),[12] alanine ($C_3H_7NO_2$),[12] oxalyldihydrazide ($C_2H_6N_4O_2$),[13] diformylhydrazine ($C_2H_4N_2O_2$),[8] tetraformaltrisazine ($C_4H_{12}N_6$),[13] and hexamethyltetramine ($C_6H_{12}N_4$).[14] Reagents without N have been also used, such as citric acid ($C_6H_8O_7$),[12] polysaccharides $(C_6H_{10}O_5)_n$,[15] and ethylene glycol ($C_2H_6O_2$).[16] The only non-carbonaceous reactive agent used

* Corresponding author. Tel.: +34 917355840; fax: +34 917355843.
E-mail address: jcfarinas@icv.csic.es (J.C. Fariñas).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.08.006

as a fuel has been hydrazine (N_2H_4).[17] These fuels differ in the reduction potential and the amount of gases they generate, thus affecting the characteristics of the reaction products. Many of these works have been devoted to compare the behaviour of some of those fuels.[10,12–15]

Some authors have stated that it was necessary to incorporate an external aid to favour the combustion reaction.[11,18] For such purpose, NH_4NO_3 has been used as an additional oxidiser. It provides an extra contribution of NO_3^-, shows highly exothermic decomposition and generates only gaseous products.[18] The addition of NH_4NO_3 increases the gases of combustion, whose effect is to expand the foam structure beyond that obtained with the metal precursors alone and eventually to increase the corresponding surface area.[9] The addition of NH_4NO_3 to the reaction mixture brings the combustion synthesis to completion rapidly and at a rather low temperature.[19]

In contrast with the variety of fuels, to the author's knowledge, there is only one paper describing the effect of two different combustion aids, NH_4NO_3 and NH_4ClO_4, both of them leading to similar results since ammonium ions liberate ammonia gas.[8]

A wide variety of single or mixed oxidic powders has been produced by combustion synthesis, but the studies on combustion synthesis of mullite are scarce. Chandran et al.[8,20] reported the synthesis of weakly crystalline mullite using aqueous heterogenerous mixtures containing aluminium nitrate and silica fume as oxidisers and either urea, carbohydrazide (CH) or diformylhydrazine (DFH) as fuels, and a rapid heating into a muffle. Fully crystalline powders were obtained by adding an extra amount of either ammonium nitrate or ammonium perchlorate as combustion aids. Ravindranathan et al.[21] compared the use of a wide variety of silicon-containing compounds such as fumed silica, tetraethylorthosilicate (TEOS), quartz, colloidal silica and tetramethylammonium silicate (TMAS) to prepare mullite by a "solid state combustion process" by using aluminium nitrate, urea and ammonium nitrate. However the necessary thermodynamic studies to control the synthesis are lacking in such works.

The combustion reaction has been classically performed in a variety of containers, such as dishes,[18] beakers,[25] crucibles,[15] and basins,[9] which are often made up of glasses,[13] although quartz,[15] alumina,[26] porcelain[18] or stainless steel[27] have been also used. To promote the ignition, the oxidiser/fuel mixture has been heated by using a hot plate (temperatures ranging from 200 to 450 °C)[15,28] or by introducing the reaction recipient into either a preheated muffle furnace (temperatures ranging from 300 to 900 °C)[14,29] or a microwave oven.[25]

In all cases, the reaction is carried out in an open recipient, where great part of the reaction product is lost as it flies out of the container during the ignition. Some strategies have been proposed to prevent this, such as covering the container with a fine-mesh sieve[30] or introducing an open borosilicate glass beaker into a closed pressure reactor under inert Ar atmosphere.[17]

In previous work, we have reported the combustion synthesis of mullite using a colloidal silica suspension.[22] The aim of the present work is to determine the role of the combustion aid in the synthesis of mullite powders through a suspension combustion process. The parameters in focus have been the design of a proper reactor, the selection of an adequate source of Si, and the evaluation of the effect of different combustion aids in the combustion process and in the characteristics of the obtained powders.

2. Experimental procedure

2.1. Reagents

For the synthesis of mullite, $Al(NO_3)_3{\cdot}9H_2O$ (analytical-reagent grade, Panreac, Spain) was used as Al source. Two sources of Si were employed, tetraethylorthosilicate (TEOS, ABCR, Germany) and a commercially available colloidal silica suspension (LEVASIL VP AC 4051, Bayer, Germany), which is supplied as an aqueous suspension with 20 wt% solids, pH 3, average particle size of 15 nm and specific surface area of 200 $m^2\,g^{-1}$. Mixtures contained 6 mole of $Al(NO_3)_3{\cdot}9H_2O$ and 2 mole of either TEOS or colloidal silica.

Urea (analytical-reagent grade, Panreac, Spain) was employed as a fuel. A reference solution was prepared on the basis of the stoichiometric molar ratio aluminium nitrate/urea (6:15). Mixtures with TEOS were prepared with additional 10, 25, and 50% mole of urea in excess over the stoichiometric ratio, while those mixtures containing colloidal silica as Si source contained 100%, and 200% in excess.

As combustion aid the following reagents were tested: NH_4NO_3, HNO_3, NH_4Cl, and H_2O_2 (analytical-reagent grade, Panreac, Spain). In all cases, a constant concentration of combustion aid of 5 mole was added.

All compounds were dissolved in pure water from a generating system (Millipore, USA) with a resistivity greater than 18 MΩ cm.

2.2. Procedure

The combustion synthesis was performed in a combustion reactor to overcome the problems associated with the combustion performed in open recipients. The combustion reactor consists of a borositicate glass reaction vessel, round bottom, flat flange, with 1000 ml capacity, provided with a lid with three ground necks. In the central neck a condenser permits the exit of the gases and avoids the condensed liquid water (and also the gases dissolved in this water) to return to the reaction vessel. By a lateral neck, a gas flow can be incorporated to change the atmosphere of the reaction. By the other lateral neck, it is possible to introduce a thermo-couple to control the temperature evolution during the reaction. The reaction system is supported on a heating mantle inside a fume-cupboard thus allowing a more uniform heating. A major advantage of this combustion reactor is that no reaction product is lost during combustion by flying out of the container.

Reaction mixtures were prepared in the reactor by mixing aluminium nitrate, urea and the proper amount of the combustion aid in the minimum amount of water necessary to obtain a good homogenisation (by 20 ml of water for near 50 g of solids). The silicon source was added in the amount required to introduce 2 mole of silica. A homogeneous aqueous suspension was achieved after stirring for a few minutes. After this, the temper-

Table 1
Reported values of formation enthalpy and specific heat of the involved compounds[23]

Compound[a]	ΔH_f° at 25 °C (kcal mol^{-1})	C_P (cal mol^{-1})
Al $(NO_3)_3{\cdot}9H_2O$ (c)	−897.57	–
SiO_2 (c)	−217.90	10.62
CO $(NH_2)_2$ (c)	−79.71	22.26
$A1_2O_3$ (c)	−400.90	$2.87+0.0773T$[b]
NH_4NO_3 (c)	−87.46	33.33
H_2O (g)	−57.80	$7.20+0.0036T$[b]
CO_2 (g)	−94.05	$10.34+0.00274T$[b]
N_2 (g)	0	$6.50+0.001T$[b]
O_2 (g)	0	$5.92+0.00367T$[b,c]
Cl_2 (g)	0	0
NH_3 (g)	−10.98	8.39
HNO_3 (l)	−41.7	26.3
H_2O_2 (l)	−44.9	21.3
NH_4Cl (c)	−75.2	20.1

[a] (c) crystalline; (g) gas; (l) liquid.
[b] T: absolute temperature.
[c] Calculated from discrete values.

ature was raised slowly to allow water evaporation and further increased to ∼300 °C in order to promote the reaction. Huge amounts of fumes were produced and, after ignition for a few seconds, a fragile foam was formed that easily crumbled into powder.

The chemical composition of the as-synthesized combustion reaction powders was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using Iris Model Thermo Jarrell Ash (USA) equipment The crystalline phases were determined by X-ray diffraction, XRD (D5000, Siemens, Germany).

Specific surface area was obtained by the one-point BET method using a Monosorb Surface Area Analyser MS-13 (Quantachrome Co., USA). The particle size distribution was determined with a laser diffraction analyser (Mastersizer S, Malvern, UK). The morphology of the powders was evaluated by scanning electron microscopy, SEM (DSM 400, Zeiss, Germany).

2.3. Thermodynamic calculations

The calculation of thermodynamic data for the combustion reactions was made by considering the formation enthalpy (ΔH_f°) and specific heat (C_p) of the compounds involved in the possible reactions that can take place. Reported values of ΔH_f° and C_p are given in Table 1.[23]

The concentration of urea for the stoichiometric reaction was calculated using the propellant criterion as described by Jain et al.[24] that considers the balance of valencies

$$\Sigma v_i n_i = 0 \quad (1)$$

where v_i and n_i are the equivalent valence and the number of Mole of each compound, respectively. To calculate the stoichiometric composition of the redox mixture, which corresponds to the release of the maximum energy for the reaction, a simple valency balance is established irrespective of whether the elements are present in the oxidizer or the fuel components of the mixture. The assumed valencies are those presented by the elements in the usual products of the combustion reaction, which are CO_2, H_2O and N_2. The extrapolation of this concept to the combustion synthesis of ceramic oxides means that metals like La and Ni (or any other metals) should also be considered as reducing elements with the valencies they have in the corresponding oxides. Considering the following valences for the elements: $C=+4$, $H=+1$, $O=-2$, $N=0$, $Al=+3$, and $Si=+4$, the oxidizing valence of $Al(NO_3)_3{\cdot}9H_2O$ is -15 and the reducing valence of urea is +6, so the stoichiometric molar ratio $Al(NO_3)_3{\cdot}9H_2O$/urea is 6/15.

Jain et al.[24] also proposed a simplified model for calculating thermochemical parameters of fuel-oxidizer mixtures by using the elemental stoichiometric coefficient (Φ_e), defined as the ratio between the composition of oxidizing and reducing elements, calculated by multiplying the corresponding coefficients by the valences of each element. A value of $\Phi_e = 1$ corresponds to the stoichiometric ratio, $\Phi_e > 1$ indicates that the mixture is fuel lean, and $\Phi_e < 1$ means that the mixture is rich in fuel.

The theoretical temperature (T) achieved during the combustion process was evaluated from data of Table 1 using Eq. (2),

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P \quad (2)$$

where ΔH is the enthalpy of each reaction and ΔC_P the specific heat of a given reaction at constant pressure. Experimental temperatures were measured with a thermocouple, although data must be taken with caution because the reaction is very fast and short (few seconds) and the contact surface is punctual and depends on how the reaction develops.

3. Results and discussion

3.1. Combustion synthesis of mullite by using TEOS as a source of Si

Table 2 shows the different reagents and amounts used for the synthesis using TEOS as a source of Si. No combustion takes place for the stoichiometric ratio (sample T1), but an excess of urea is necessary for the reaction to occur, which is accompanied by a strong decrease of the surface area of the resulting powder.

Fig. 1 compares the XRD pattern of samples T1 and T4 (stoichiometric and 50% excess of urea, respectively). The XRD spectra of samples T2 and T3 are similar to that of T4. Sample

Table 2
Reagents and concentrations used for the synthesis using TEOS as a source of Si and characteristics of the as-synthesized powders

Reaction mixture	T1	T2	T3	T4
Excess of $CO(NH_2)_2$				
wt%	0	10	25	50
mole	0	1.5	3.75	7.5
Combustion	No	Yes	Yes	Yes
S_s ($m^2\,g^{-1}$)	145	52	21	27
D_{50} (μm)	68	29	45	65

Mixtures were prepared with 2 mole of TEOS and 6 mole of Al $(NO_3)_3{\cdot}9H_2O$.

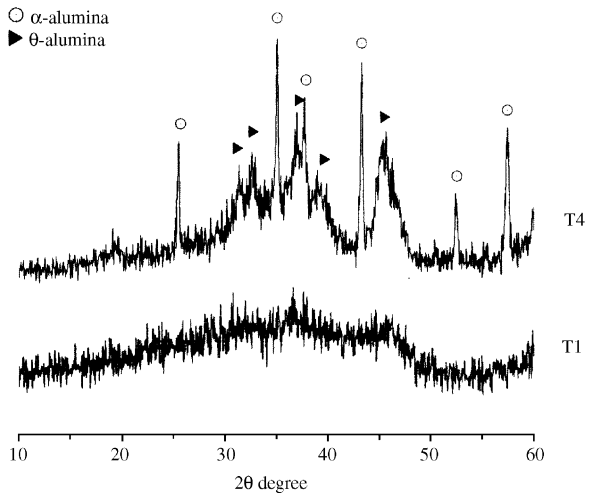

Fig. 1. XRD patterns of powders obtained with TEOS in the stoichiometric ratio (sample T1) and with 50% in excess (sample T4).

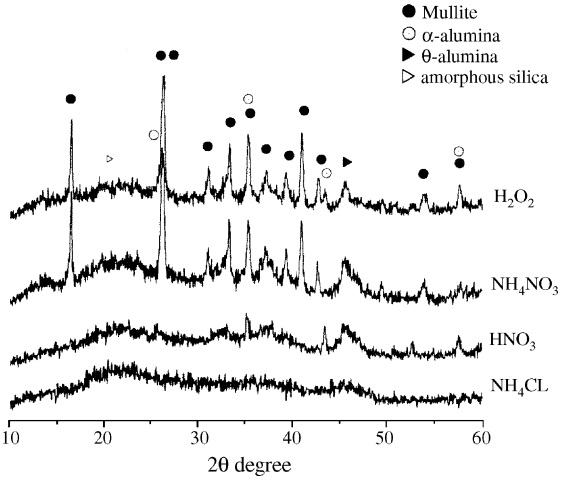

Fig. 2. XRD patterns of as-synthesized powders produced with the different combustion aids and 100% excess of urea (samples S1, S2, S3 and S4).

T1 leads to an amorphous spectrum as no combustion reaction occurred. In the case of sample T4, combustion took place and crystalline phases were registered in the XRD pattern. However, the only peaks appearing in the spectrum were those corresponding to both α-Al_2O_3 and θ-Al_2O_3 but there was no evidence of the presence of remaining silica. Chemical analysis of the final products of the different reactions performed by ICP-AES demonstrates that the concentration of SiO_2 was as low as 1 wt%, as summarized in Table 3, for samples T1 and T3. This means that silicon is lost during the reaction, which is probably associated with the evaporation of TEOS (boiling point 165 °C) on heating before hydrolysis.

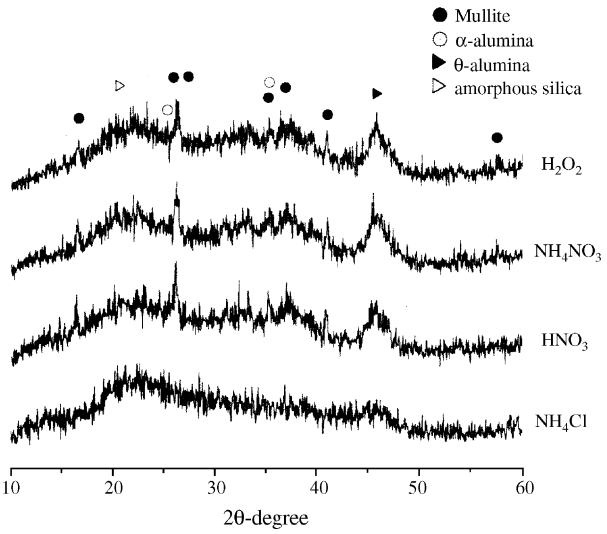

Fig. 3. XRD patterns of as-synthesized powders produced with the different combustion aids and 200% excess of urea (samples S5, S6, S7 and S8).

Table 3
Chemical analysis by ICP-AES of the major components of various as-prepared samples

Reaction mixture	$A1_2O_3$ (wt%) (±0.8)	SiO_2 (wt%) (±0.3)
T1	98.9	1.1
T3	99.1	0.9
S1	72.8	27.2
S2	72.2	27.8
S4	71.2	28.8
S7	71.5	28.5

Stoichiometric Al_2O_3/SiO_2 mass ratio is 71.8/28.2.

3.2. Combustion synthesis of mullite by using colloidal silica suspension as a source of Si

Previous work[22] reported the combustion synthesis of mullite using aluminium nitrate as Al source, colloidal silica suspension

Table 4
Equations describing the total reactions that could occur during combustion with different combustion aids and their calculated enthalpies

Reaction	Describing equation	ΔH_f° at 25 °C (kcal mol^{-1})
R1	$6Al(NO_3)_3{\cdot}9H_2O$ (c) + $2SiO_2$ (c) + $m CO(NH_2)_2$ (c) + $(1.5m - 22.5)O_2$ (g) → $Al_6Si_2O_{13}$ (c) + $(54 + 2m)H_2O$ (g) + $(9 + m)N_2$ (g) + mCO_2 (g)	$2673.22 - 129.9m$
R2	$6Al(NO_3)_3{\cdot}9H_2O$ (c) + $2SiO_2$ (c) + $m CO(NH_2)_2$ (c) + $n NH_4NO_3$ (c) + $(1.5m - 22.5 - 1.25n)O_2$ (g) → $Al_6Si_2O_{13}$ (c) + $(54 + 2m + 0.5n)H_2O$ (g) + nNH_3 (g) + mCO_2 (g) + $(9 + m + 0.5n)N_2$ (g)	$2673.22 - 129.9m + 47.6n$
R3	$6Al(NO_3)_3{\cdot}9H_2O$ (c) + $2SiO_2$ (c) + $m CO(NH_2)_2$ (c) + $2p HNO_3$ (l) + $(1.5m - 22.5 - 2.50p)O_2$ (g) → $Al_6Si_2O_{13}$ (c) + $(54 + 2m + p)H_2O$ (g) + mCO_2 (g) + $(9 + m + p)N_2$ (g)	$2673.22 - 129.9m + 25.6p$
R4	$6Al(NO_3)_3{\cdot}9H_2O$ (c) + $2SiO_2$ (c) + $m CO(NH_2)_2$ (c) + $q NH_4Cl$ (s) + $(1.5m - 22.5)O_2$ (g) → $Al_6Si_2O_{13}$ (c) + $(54 + 2m)H_2O$ (g) + mCO_2 (g) + $(9 + m)N_2$ (g) + $0.5qH_2$ + $0.5qCl_2$ + qNH_3 (g)	$2673.22 - 129.9m + 64.22q$
R5	$6Al(NO_3)_3{\cdot}9H_2O$ (c) + $2SiO_2$ (c) + $m CO(NH_2)_2$ (c) + $r H_2O_2$ (1) + $(1.5m - 22.5 - 0.5r)O_2$ (g) → $Al_6Si_2O_{13}$ (c) + $(54 + 2m + r)H_2O$ (g) + mCO_2 (g) + $(9 + m)N_2$ (g)	$2673.22 - 129.9m + 12.90r$

Table 5
Combustion aids used for the synthesis of mullite using colloidal silica suspension as source of Si, and calculated values of elemental stoichiometric coefficient (Φ_e) and theoretical temperature (T) achieved during the combustion process

Reaction mixture	S1	S2	S3	S4	S5	S6	S7	S8
CO $(NH_2)_2$ %excess	100	100	100	100	200	200	200	200
Combustion aid (5 mol)	NH_4NO_3	HNO_3	NH_4Cl	H_2O_2	NH_4NO_3	HNO_3	NH_4Cl	H_2O_2
Φ_e	0.71	0.76	0.62	0.68	0.57	0.59	0.51	0.56
T (°C)	581	638	548	1011	1176	1212	1166	1249

Mixtures were prepared with 2 mole of silica and 6 mole of $Al(NO_3)_3{\cdot}9H_2O$.

as Si source, urea as fuel, and ammonium nitrate as a combustion aid. In the present work the effect of different combustion aids on the efficiency of the synthesis is studied while maintaining the same reagents and fuel (urea, in concentrations of 100 and 200% in excess). Besides ammonium nitrate, which is the most commonly used combustion aid, nitric acid (HNO_3), ammonium chloride (NH_4Cl) and H_2O_2 were also tested and compared to the reference compound. HNO_3 is used to supply NO_3^- and NH_4Cl supplies NH_4^+, whereas H_2O_2 is a source of O_2 in the nascent state. In addition to the ions supplied it is crucial to consider the reduction potential of such additives. The standard reduction potential for HNO_3 and NH_4NO_3 is the same (0.957 eV), while that of H_2O_2 is higher (1.776 eV). However, the NH_4Cl is a reductor agent.

The enthalpy involved in the reactions occurring with every combustion aid can be calculated from the thermodynamic data listed in Table 1. The equations describing the combustion reactions and the calculated enthalpies are reported in Table 4.

From a thermodynamic point of view, the addition of urea in excess supplies the heat needed for the combustion reaction and determines the theoretical temperature of the reaction. Table 5 shows the calculated values of the elemental stoichiometric coefficients (Φ_e) and the theoretical temperature (T) achieved during the reactions using different combustion aids and colloidal silica suspension as a source of Si.

The theoretical temperatures expected when the excess of urea is 200% is nearly twice that corresponding to 100% excess of urea, except in the case of H_2O_2. In the latter case the theoretical temperature of the reaction is much higher than for the other aids, and the relative increase when the excess of urea is doubled is roughly 20%. Comparing the other combustion aids, it can be seen that the acid leads to slightly higher temperature than the salts. The values of the coefficient (Φ_e) are higher for 100% excess of urea, but maintain always $\Phi_e < 1$, since all mixtures are rich in fuel.

All reaction mixtures led to combustion with flame, excepting that involving NH_4Cl and 100% excess of urea (sample S3), as summarized in Table 6. When HNO_3 was added the formation of foam was very low. On the other hand, the chemical composition of all the as-prepared powders corresponds to that of mullite, as can be seen in Table 3 for samples S1, S2, S4 and S7.

Fig. 2 plots the XRD patterns of as-synthesized powders produced with the different combustion aids and 100% excess of urea (samples S1, S2, S3 and S4). When NH_4Cl is used (sample S3), an amorphous XRD diagram is obtained, with a broad, low intensity signal that suggests the presence of unreacted silica This fact can explain the higher specific surface area of this powder (Table 6). When using HNO_3 (sample S2) some low intensity peaks appear that correspond to α-Al_2O_3 and θ-Al_2O_3. None of these aids leads to the direct formation of mullite. When either H_2O_2 or NH_4NO_3 are added, a quite different XRD pattern is obtained, where both α-Al_2O_3 and θ-Al_2O_3 are present, as well as crystalline mullite. In both cases the characteristic broad peak of amorphous SiO_2 can be still detected.

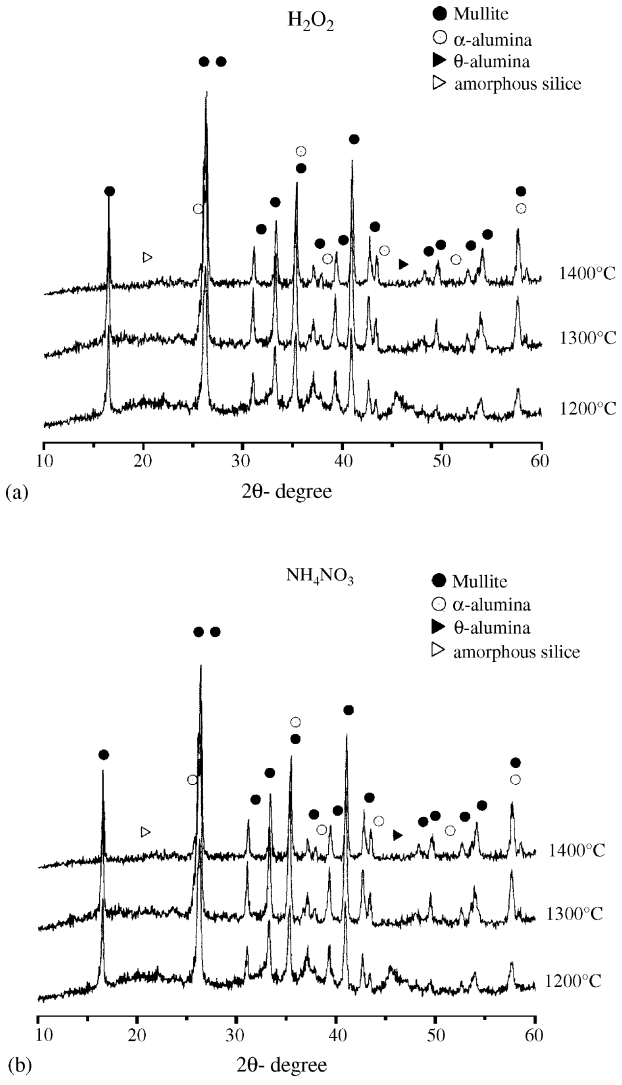

Fig. 4. XRD patterns of powders produced with 100% excess of urea and NH_4NO_3 (a) and H_2O_2 (b) after calcining at 1200, 1300 and 1400 °C.

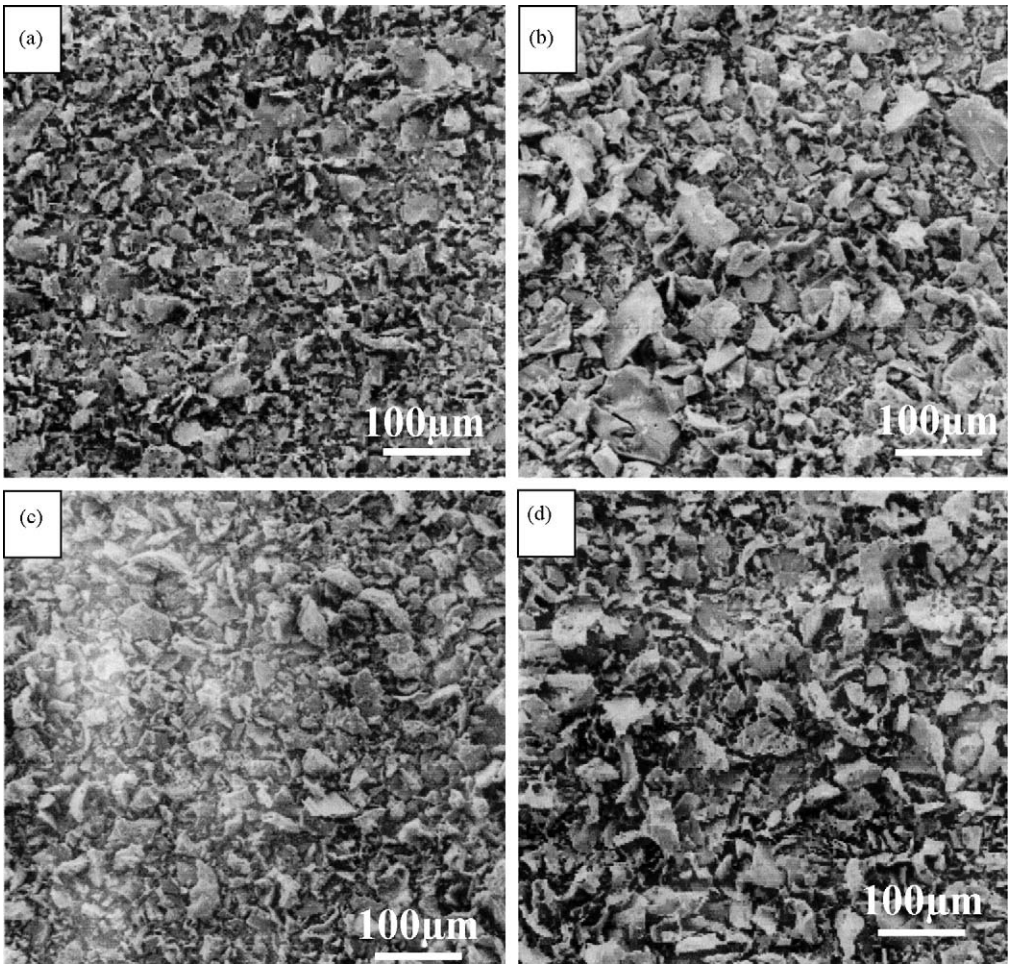

Fig. 5. SEM pictures of powders produced with 100% excess of urea and NH_4NO_3 (a), HNO_3 (b), NH_4Cl (c), and H_2O_2 (d), at low magnification.

Fig. 3 plots the XRD patterns corresponding to the as-synthesized powders produced with 200% excess of urea (samples S5, S6, S7 and S8). In this case the XRD patterns show that crystallinity is very much lower and the mullite phase is not clearly detected. This can be attributed to the fact that the quantity of urea in excess is so large that reaction becomes more rapid so that there is no time enough to complete the reaction.

According to these results, mullite appears after the combustion reaction without any further thermal treatment when either H_2O_2 or NH_4NO_3 are used as combustion aid in the presence of 100% excess of urea. In order to explain the effect of the combustion aids, the standard reduction potential must be considered, as well as the volume and nature of gases generated during reactions. The fact that combustion successfully occurs with H_2O_2 can be explained by considering its highest reduction potential, the consequence being a higher crystallinity in the as-synthesized powder. Taking into account the reduction potentials, it must be expected that no reaction occurs for NH_4Cl, and both HNO_3 or NH_4NO_3 should give a similar result. When compared, NH_4NO_3 forms larger volume of gases with increased reactivity, which promotes the formation of strongly reactive foam that increases the availability of reaction sites between reagents because of its higher surface area.

According to calculated theoretical temperatures (Table 5), reactions with NH_4Cl, HNO_3, and NH_4NO_3 would occur at quite similar temperature (548, 638 and 581 °C, respectively). The temperatures measured experimentally with the thermocouple were 464, 1044 and 551 °C, respectively. For the salts, there is a good agreement between the theoretical and the experimental temperatures, whereas HNO_3 gives an experimental temperature much higher than predicted. In this case, the foam formed during the reaction was smaller and thus, more error is made when introducing the thermocouple because of the lack of homogeneity in the contact surface. On the other hand, NH_4Cl and

Table 6
Results of the combustion process using colloidal silica suspension as source of Si and characteristics of the obtained powders

Reaction mixture	S1	S2	S3	S4	S5	S6	S7	S8
Combustion	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes
S_s ($m^2\ g^{-1}$)	28	46	248	59	85	61	153	230
D_{50} (μm)	82	61	71	123	83	85	141	168

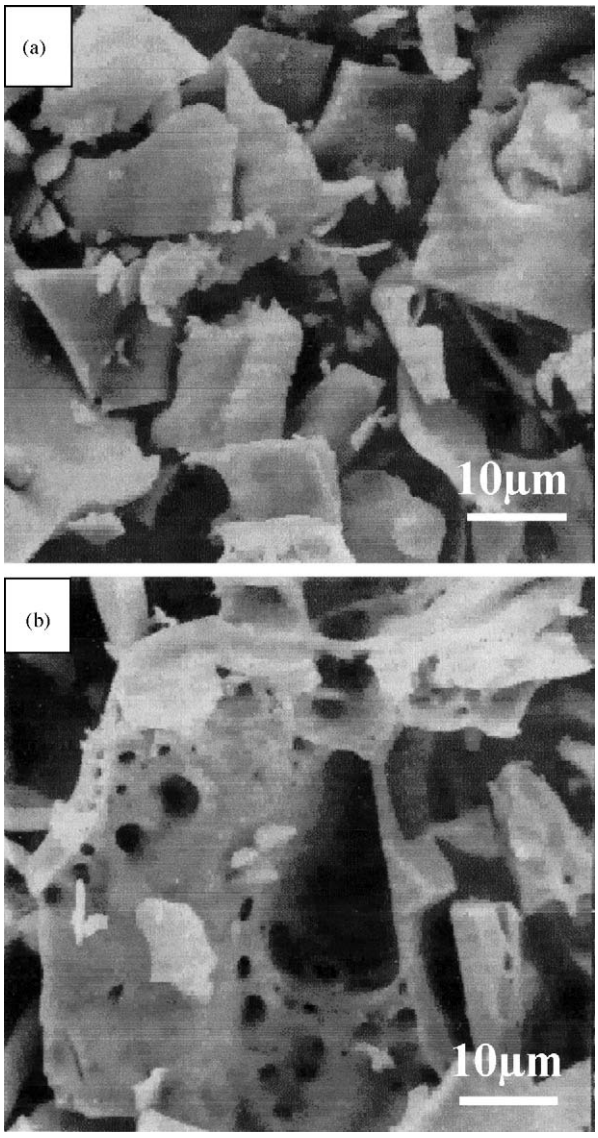

Fig. 6. SEM pictures of powders produced with 100% excess of urea and NH_4NO_3 (a) and H_2O_2 (b), at high magnification.

NH_4NO_3 have no great differences in either the theoretical or the experimental temperature, although mullite is only formed with the latter. This demonstrates that the success of the combustion reaction not only depends on the temperature of the reaction.

On the other hand, mullite is better formed with H_2O_2, whose theoretical temperature is much higher (1011 °C). Direct observation of the reactions demonstrates that the reaction with H_2O_2 is vigorous and ignition prolongs for longer times, although the experimental temperature is 760 °C, lower than the calculated one. The volume of gases generated with H_2O_2 is large, but the molecular volume is lower than that of ammonia molecules. As a result, the volume of foam for this reaction is much lower than that generated with NH_4Cl and NH_4NO_3.

Consequently, the propellant criterion usually employed to explain the thermodynamics of the combustion is not capable itself to explain the formation of mullite with H_2O_2.

A study of the thermal evolution of the as-synthesized powders in which mullite phase is detected, was carried out. Samples S1 and S4 were subjected to thermal treatments at temperatures of 1200, 1300 and 1400 °C in order to improve their crystallinity. The corresponding XRD patterns are shown in Fig. 4. At 1300 °C, a good crystallinity is reached with a significant decrease of the broad peak of SiO_2 but complete crystallinity of mullite is reached at 1400 °C, where θ-Al_2O_2 and SiO_2 signals disappear, due to the reaction of both oxides in solid state in the temperature range of 1250–1400 °C.

SEM pictures of powders synthesized with 100% excess of urea and with the four additives are shown in Fig. 5. The SEM microstructure at higher magnification of samples obtained with NH_4NO_3 (S1) and H_2O_2 (S4) is shown in Fig. 6. In all cases a porous structure with plate-like morphology is obtained, similar to that obtained in other works. The differences in the amount and size of pores depend on the number of mole and the nature of gases generated during combustion. The average particle size in sample S4 is by 120 μm while that of sample S1 is by 80 μm (Table 6), which may be explained by considering that the temperature reached in the reaction is higher that achieved in sample S1 and thus, the formation of sintering necks is favoured. The surface area of sample S4 is twice that of sample S1. This is in agreement with the appearance of the obtained particles, which contain a larger amount of pores than powders of sample S1, as can be observed in the higher magnifications pictures of Fig. 6. When the excess of urea is 200% a larger volume of gases is retained that increases the surface area more rapidly than the particle size.

4. Conclusions

A combustion reactor has been designed that permits the synthesis of powders with some advantages as compared to the classical procedures (heating of an open recipient in a hot-plate, a furnace or a microwave oven). Mullite powders with a high specific surface area and a high compositional homogeneity can be successfully synthesized by a single step combustion process using a silica suspension as a source of Si. The influence of the combustion aid has been studied by comparing different agents, namely NH_4NO_3, HNO_3, NH_4Cl and H_2O_2. From thermodynamic considerations, an overall reaction for all species involved in the process is proposed.

According to thermodynamic considerations, the temperatures for reactions with HNO_3 and NH_4NO_3 are similar but no crystalline mullite is obtained with the first. This demonstrates that the success of the combustion reaction not only depends on the temperature of the reaction. NH_4NO_3 is considered a suitable combustion aid because it behaves as an oxidant and allows the formation of a reactive foam whose high surface area improves reactivity. This work demonstrates that NH_4NO_3 can be adequately replaced by H_2O_2 as a combustion aid because H_2O_2 has a strong reduction potential, as it supplies nascent oxygen. However, from enthalpy predictions H_2O_2 would not give crystalline mullite as an additional strong heat supply should be given.

The propellant criterion has been widely employed to predict the thermodynamics of the combustion reactions, but there are

no works reporting the calculations for a system with combustion aids with large differences in the reduction potential. The propellant criterion is not capable itself to explain the formation of mullite with H_2O_2 performed in this work as it does not consider other parameters behind the calculations of enthalpy (i.e., the reduction potential).

Acknowledgement

This work has been supported by CICYT, Spain (Contract MAT2003-00836).

References

1. Somiya, S., Davies, R. F. and Pask, J. A. ed., *Mullite and Mullite Matrix Composites, Ceramic Transactions*, *6*. American Ceramic Society, Westerville, OH, USA, 1990.
2. Aksay, I. A., Dabbs, D. M. and Sarikaya, M., Mullite for structural, electronic, and optical applications. *J. Am. Ceram. Soc.*, 1991, **74**(10), 2343–2358.
3. Sacks, M. D., Lee, H. W. and Pask, J. A., A review of powder preparation methods and densification procedures for fabricating high density mullite. In *Mullite and Mullite Matrix Composites, Ceramic Transactions*, *6*, ed. S. Somiya, R. F. Davies and J. A. Pask. The American Ceramic Society Inc., Westerville, OH, USA, 1990, pp. 167–207.
4. Sonupaslak, B., Sol–gel processing of infrared transparent mullite. *Adv. Ceram. Mater.*, 1988, **3**(3), 263–267.
5. Lee, J. E., Kim, J. W., Jung, Y. G., Jo, C. Y. and Paik, U., Effect of precursor pH and sintering temperature on synthesizing and morphology of sol-gel processed mullite. *Ceram. Int.*, 2002, **28**(8), 935–940.
6. Tang, Y. F., Feng, L., Chen, Y. F. and Li, A. D., Fabrication of mullite powders by a novel processing. *Adv. Eng. Mater.*, 2004, **6**(1–2), 69–71.
7. Patil, K. C., Aruna, S. T. and Mimani, T., Combustion synthesis: an update. *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 507–512.
8. Chandran, R. G., Chandrashekar, B. K., Ganguly, C. and Patil, K. C., Sintering and microstructural investigations on combustion processed mullite. *J. Eur. Ceram. Soc.*, 1996, **16**(8), 843–849.
9. Segadães, A. M., Morelli, M. R. and Kiminami, R. G. A., Combustion synthesis of aluminium titanate. *J. Eur. Ceram. Soc.*, 1998, **18**(7), 771–781.
10. Jung, C. H., Park, J. Y., Oh, S. J., Park, H. K., Kim, Y. S., Kim, D. K. *et al.*, Synthesis of Li_2TiO_3 ceramic breeder powder by the combustion process. *J. Nucl. Mater.*, 1998, **253**, 203–212.
11. Aruna, S. T. and Rajam, K. S., Mixture of fuels approach for the solution combustion synthesis of Al_2O_3–ZrO_2 nanocomposite. *Mater. Res. Bull.*, 2004, **39**, 157–167.
12. Li, F., Hu, K., Li, J., Zhang, D. and Chen, G., Combustion synthesis of γ-lithium aluminate by using various fuels. *J. Nucl. Mater.*, 2002, **300**, 82–88.
13. Suresh, K., Panchapagesan, T. S. and Patil, K. C., Synthesis and properties of $La_{1-x}Sr_xFeO_3$. *Solid State Ionics*, 1999, **126**, 299–305.
14. Patro, P. K., Kulkarni, A. R. and Harendranath, C. S., Combustion synthesis of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ and effect of fuel on its microstructure and dielectric properties. *Mater. Res. Bull.*, 2003, **38**, 249–259.
15. Macedo, Z. S., Ferrari, C. R. and Hemandes, A. C., Self-propagation high-temperature synthesis of bismuth titanate. *Powder Technol.*, 2004, **139**, 175–179.
16. Dasgupta, N., Krishnamoorthy, R. and Jacob, K. T., Glycol-nitrate combustion synthesis of fine sinter-active yttria. *Int. J. Inorg. Mater.*, 2001, **3**, 143–149.
17. Garcia, R., Hirata, G. A. and McKittrick, J., New combustion synthesis technique for the production of $(In_xGa_{1-x})_2O_3$ powders: hydrazine/metal nitrate method. *J. Mater. Res.*, 2001, **16**(4), 1059–1065.
18. Civera, A., Pavese, M., Saracco, G. and Specchia, V., Combustion synthesis of perovskite-type catalysts for natural gas combustion. *Catal. Today*, 2003, **83**, 199–211.
19. Biamino, S. and Badini, D., Combustion synthesis of lanthanum chromite starting from water solutions: investigation of process mechanism by DTA-TA-MS. *J. Eur. Ceram. Soc.*, 2004, **24**, 3021–3034.
20. Chandran, R. G. and Patil, K. C., A rapid combustion process for the preparation of crystalline mullite powders. *Mater. Lett.*, 1990, **10**(6), 291–295.
21. Ravindranathan, P., Komarneni, S. and Roy, R., Synthesis of lithium aluminate, mullite and colored zirconia by a combustion process. *J. Mater. Sci. Lett.*, 1993, **12**(6), 369–371.
22. Burgos-Montes, O., Moreno, R., Colomer, M. T. and Fariñas, J. C. Synthesis of mullite powders through a suspension combustion process. *J. Am. Ceram. Soc.*, in press.
23. *Handbook of Chemistry and Physics* (84th ed.), ed. D. R. Lide. CRC Press, USA, 2003–2004.
24. Jain, S. R., Adiga, K. C. and Pai Verneker, V. R., A new approach to thermochemical calculations of condensed fuel-oxidizer mixtures. *Combust. Flame*, 1981, **40**, 71–79.
25. Chung, D. Y. and Lee, E. H., Microwave-induced combustion synthesis of $Ce_{1-x}Sm_xO_{2-x/2}$ powder and its characterization. *J. Alloy Compd.*, 2004, **374**(1–2), 69–73.
26. Hwang, C., Wu, T., Wan, J. and Tsai, J., Development of a novel combustion synthesis method for synthesizing of ceramic oxide powders. *Mater. Sci. Eng. B*, 2004, **111**, 49–56.
27. Panitz, J., Mayor, J., Grob, B. and Durisch, W., A Raman spectroscopic study of rare earth mixed oxides. *J. Alloy Compd.*, 2000, **303–304**, 340–344.
28. Purohit, R. D., Sharma, B. P., Pillai, K. T. and Tyagi, A. K., Ultrafine ceria powders via glycine–nitrate combustion. *Mater. Res. Bull.*, 2001, **36**, 2711–2721.
29. Aruna, S. T., Muthuraman, M. and Patil, K. C., Studies on combustion synthesized $LaMnO_3$–$LaCoO_3$ solid solutions. *Mater. Res. Bull.*, 2000, **35**, 289–296.
30. Potdar, H. S., Deshpande, S. B., Khollam, Y. B., Deshpande, A. S. and Date, S. K., Synthesis of nanosized $Ce_{0.75}Zr_{0.25}O_2$ porous powders via an autoignition: glycine nitrate process. *Mater. Lett.*, 2003, **57**, 1066–1071.