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Preparation and characterization of lanthanum zirconate

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Lanthanum zirconate has been prepared by citrate synthesis, by coprecipitation and by solid state decomposition of metal nitrate–urea mixtures. The relative advantages of these methods with respect to surface area and reproducibility are investigated. The lanthanum zirconate phase is formed by the urea decomposition method without any additional heat treatment. In the case of the citrate and coprecipitation methods the pyrochlore phase is formed only after heating the precursor above 900 °C. The citrate method yields the highest surface area, the coprecipitation method gives more reproducible results. However, after washing with ethanol the coprecipitated sample has much higher surface area compared with the citrate method. © *1998 Kluwer Academic Publishers*

1. Introduction

High temperature materials are currently attracting considerable interest in the field of heterogeneous catalysis. For catalytic applications at high temperatures, like total combustion of methane, the material should have a high melting point, an ability to withstand reducing and oxidizing atmospheres, good hydrothermal stability and a stable surface area with as high a value as possible. Rare-earth pyrochlores are refractory materials with very high melting points (> 2000 °C) [1]. The crystal structure of lanthanum zirconate is unique, and allows for numerous ionic substitutions at various lattice points, producing a large number of compounds with different thermal, electrical and catalytic properties [1].

The performance of the final product depends very much on the synthesis procedure and conditions. Different methods can be used to prepare these materials and these include solid state mixing of powders, solution routes using organic and inorganic precursors, an ion exchange method using molten nitrate salts, and hydrothermal routes [2–5]. Three methods were selected for investigation in this work: the citrate method; flash decomposition of a urea–nitrate mixture, and coprecipitation. The main reason for selecting the above methods is that they are relatively simple and do not involve any complex experimental set up.

Van de Graaf *et al.* [6] have reported that it is possible to obtain very fine homogeneous particles using the citrate route. This method involves complexing the metal ions, present as nitrates in solution, with excess citric acid, neutralizing the solution with ammonia and finally evaporating the solvent and pyrolysing the residue. The powder is then calcined at the temperature required.

Kingsley and Patil [7] have used the second method to prepare submicrometre-sized alumina and zirconia–alumina mixtures. Recently they have extended this technique for the preparation of rare-earth zirconates [8]. The method involves a combustion process using metal nitrate–urea mixtures; the product is formed within a very short reaction time without further calcination. The exothermic character of the reaction is responsible for the successful formation of the oxides.

The third method, coprecipitation, has been found to be an effective method in the preparation of catalysts. It allows the preparation of powders with uniform composition on a nanostructure level and involves different variables such as the concentration of the precursor, the pH of precipitation, washing procedure, ageing, drying etc. Varying any one of these parameters will have a profound effect on the performance of the final product.

This paper describes the synthesis of lanthanum zirconate using these different routes. The resultant powders have been characterized by various techniques to examine the effect of the preparation method

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on the surface area and to determine the reproducibility of the methods.

2. Experimental procedures

The chemicals used were lanthanum nitrate, $La(NO_3)_3 \cdot 6H_2O$ (Merk), zirconyl oxynitrate $ZrO(NO_3)_2 \cdot XH_2O$ (Janssen chimica), citric acid (Merk), urea (Fluka), zirconyl chloride octahydrate $ZrOCl_2 \cdot 8H_2O$ (Merk) and ammonia.

2.1. Preparation of the precursors

Stoichiometric amounts of the two nitrate solutions were thoroughly mixed and the required amounts of citric acid (mono hydrate) were then added in equivalent amounts. Concentrated ammonia solution was then added dropwise to the mixture, with constant stirring, until the pH reached 7($\pm$ 0.3) [6]. The solution was then heated in a 2 l beaker on a hot plate. During heating, it boiled and the solvent evaporated; a viscous residue was then formed, which suddenly decomposed by spontaneous combustion giving a dull black, homogeneous, foamy mass. This was powered (referred to as CIT) and calcined at temperatures ranging from 700 to 1200 °C.

For the preparation of lanthanum zirconate by the flash-combustion technique, stoichiometric amounts of the metal nitrates and urea were mixed thoroughly with distilled water in an agate mortar. The resultant paste was then transferred to a pyrex dish and heated on a hot plate. The paste rapidly boiled, melted and underwent dehydration, followed by decomposition, with the evolution of large amounts of the oxides of nitrogen and ammonia. It then frothed, foamed and ignited spontaneously, burning with a white flame, and a white fluffy powder resulted. The powder was ground (referred to as FCT) and then calcined at different temperatures ranging from 900 to 1200 °C.

For the preparation of the sample through co-precipitation, solutions of stoichiometric amounts of lanthanum nitrate and zirconyl oxychloride, both at concentrations of 0.5 mol dm^{-3}, were mixed thoroughly. The resultant mixture was added dropwise at a rate of 50 cm^3 min^{-1}, together with a solution of ammonia, to doubly distilled water, the pH of which was adjusted to 10 with ammonia. During the whole process, the pH was kept at 10 ($\pm$ 0.15) by adjusting the flow of ammonia. The white precursor was then aged in the mother liquor for 24 h and the resultant gelatinous precipitate was washed thoroughly with a distilled water–ammonia mixture (reducing the ammonia concentration as washing progressed) to obtain a material free of chloride and nitrate ions. Both precipitation and redispersion were carried out in a special type of reactor reported by van de Graff *et al.* [9]. During these processes the mixture was stirred vigorously to achieve a maximum degree of dispersion. For comparison, a small portion of the water-washed sample was further washed with ethanol. The precipitates were then dried in an oven in static air at 110 ° for 24 h and were dry-milled (referred to as CPT) and subsequently calcined at different temperatures from 600 to 1200 °C.

To check the reproducibility of these preparation methods experiments were repeated at least three times.

2.2. Calcination procedure

Calcinations were carried out at different temperatures ranging from 600 to 1200 °C in air for 4 h. To see the phase formation in the case of the citrate method the precursor was calcined at 700 °C for 66 h. The samples were heated at a rate of 3 °C min^{-1} to the required temperature, kept there for the required time and then cooled at a rate of 3 °C min^{-1} to 200 °C. In each case, samples of approximately 4 g were heated in alumina crucibes.

2.3. Characterization techniques

The thermal decomposition characteristics of the different samples were studied both in air and in nitrogen using alumina cups with a Stanton Redcroft differential scanning calorimeter (DSC 1500). Simultaneous thermogravimetric (TGA) and differential thermal analyses (DTA) were performed in air using a Polymer Lab, Thermal Science System, with platinum cups as sample holders. All the thermal analyses experiments were performed at a heating rate of 10 °C min^{-1}.

Infra-red (i.r.) spectra in the transmission mode were obtained using a Nicolet 20 SXB Fourier transform intra-red (FTR) spectrometer, using KBr as the reference material.

X-ray diffraction (XRD) patterns of the material after each heat treatment were recorded with a Phillips PW 1710 X-ray diffractometer using nickel-filtered CuK_α radiation. Continuous scans in the range 20–70 ° were used.

Raman spectra were recorded on a SPEX-Triplemate spectrometer equipped with an EGG multichannel detector. The laser source was a Spectra Physics Ar^+ laser operating at a wavelength of 514.5 nm using 25 mW laser power at the spot.

Surface area measurements of the different samples were determined by analysis of adsorption isotherms of nitrogen at liquid nitrogen temperature using a Micromeritics ASAP 2400 system. All the samples were degassed at a temperature of 150 °C for 16 h prior to the measurements.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the decomposition behaviour of the citrate precursor (CIT) during calcination in the thermal analysis system. There are two exothermic peaks present in the DTA trace at 420 and 532 °C. These peaks correspond to weight losses as seen from the TGA and DTG. The two exothermic peaks may be attributed to the decomposition of the citrate complex including decarboxylation with the evolution of CO and CO_2. Srivastava and Dongare [10] have studied the decomposition behaviour of zirconia precursors

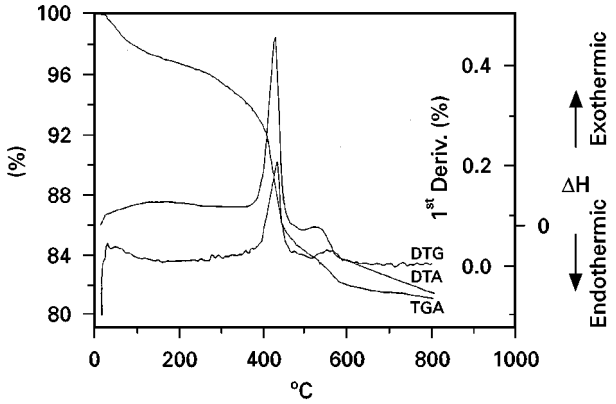

Figure 1 DTA, TGA and DTG traces of lanthanum zirconate gel prepared through the citrate route.

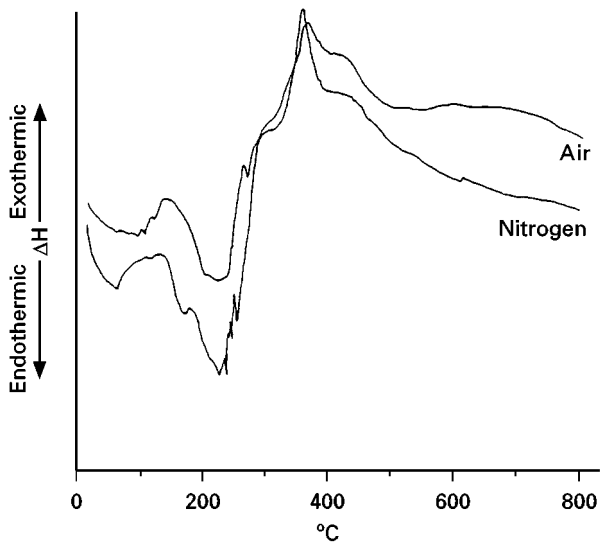

Figure 2 DSC traces of lanthanum zirconate flash combustion precursor heated in air and nitrogen.

prepared by the citrate method and they also observed these two peaks. The decomposition of metal citrate complexes has been described [11] as being endothermic, even when the decomposition takes place in air. The reason for this is not known at this moment.

The DSC curves of flash-combustion precursors (i.e. a mixture of zirconyl oxynitrate, lanthnum nitrate and urea in stoichiometic ratio) in both air and nitrogen are given in Fig. 2. There is a large exothermic peak (both in air and nitrogen) at 380 °C. The flash combustion method is a solid state combustion process, which involves explosive decomposition of nitrate–urea mixtures. When pure urea is heated, it decomposes into biuret ($C_2H_3H_5O_2$) and then to the $(HNCO)_3$ trimer and this is followed by the liberation of ammonia [12]. When lanthanum nitrate is heated, it undergoes dehydration followed by decomposition into its oxide and the oxides of nitrogen [13]. Zirconyl oxynitrate also decomposes into its oxide above 500 °C [13]. By heating the urea–nitrate mixture, all these reactions seem to occur simultaneously because of the large amount of heat evolved, which is followed by a temperature rise. The exothermic reaction may be due to the oxidative decomposition of urea, which acts as a fuel. In this situation, the local temperature will suddenly go up

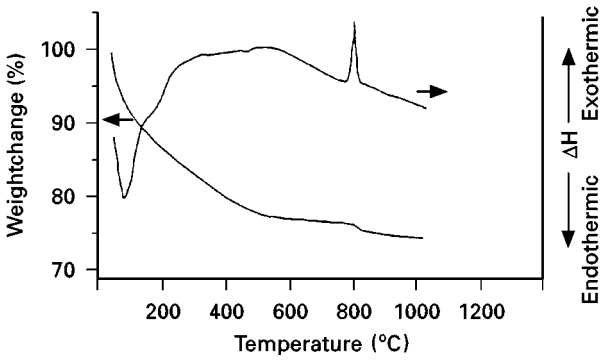

Figure 3 DTA, TGA and DTG traces of lanthanum zirconate gel prepared through coprecipitation.

and the whole reaction will be over within a few minutes. The observation that the powder after flash combustion (without any further heat treatment) shows the X-ray pattern of $La_2Zr_2O_7$, which is normally formed only at higher temperatures, support the fact that high local temperatures are reached during the flash decomposition reaction. The DSC curves of the reaction both in air and nitrogen show similar behaviour (Fig. 2). This indicates that the reaction proceeds exothermically both in air and nitrogen and thus it can be inferred that it is auto oxidizing in nature.

The results of thermal analysis (DTA and TGA) of the gel prepared through coprecipitation (CPT) are shown in Fig. 3. The TGA trace shows two regions of significant weight loss, one centred around 80 °C, corresponding to the loss of physically adsorbed water in the porous gel network, and the other centred around 300 °C, corresponding to the removal of the hydroxyl groups. The TGA curve is typical of the behaviour of gels in which dehydration occurs continuously over the whole range of temperature studied [14–16]. The exothermic peak at around 812 °C in the DTA curve is probably due to the crystallization of the amorphous gel and is also accompanied by a small weight loss.

3.2. Infrared spectra

Fig. 4 shows i.r. spectra of the citrate precursor (CIT) heated at different temperatures. The broad band in the range 3500–3000 cm^{-1} for all the samples is due to the presence of water, the intensities of this band were found to decrease with the temperature at which the material had been calcined. The intensities of the absorption bands at 1500, 1400 and 850 cm^{-1}, due to the presence of carboxylate groups [10, 11], also decreased as the temperature was increased. The absorption band at 510 cm^{-1}, which appeared for temperatures above 900 °C was due to lattice vibration of the Zr–O stretching vibrations of the lanthanum zirconate [1], and this became stronger after the sample had been heated at 1000 °C. The i.r. spectra of the as-flashed (FCT) powder was similar to that of the citrate precursor calcined above 900 °C.

3.3. XRD studies

Representative XRD patterns of the powder obtained by flash combustion but without any further heat

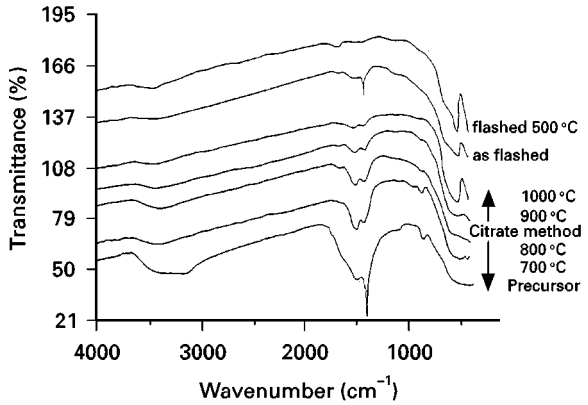

Figure 4 IR spectra of lanthanum zirconate prepared through citrate route after heating at different temperatures and the sample prepared through flash decomposition technique.

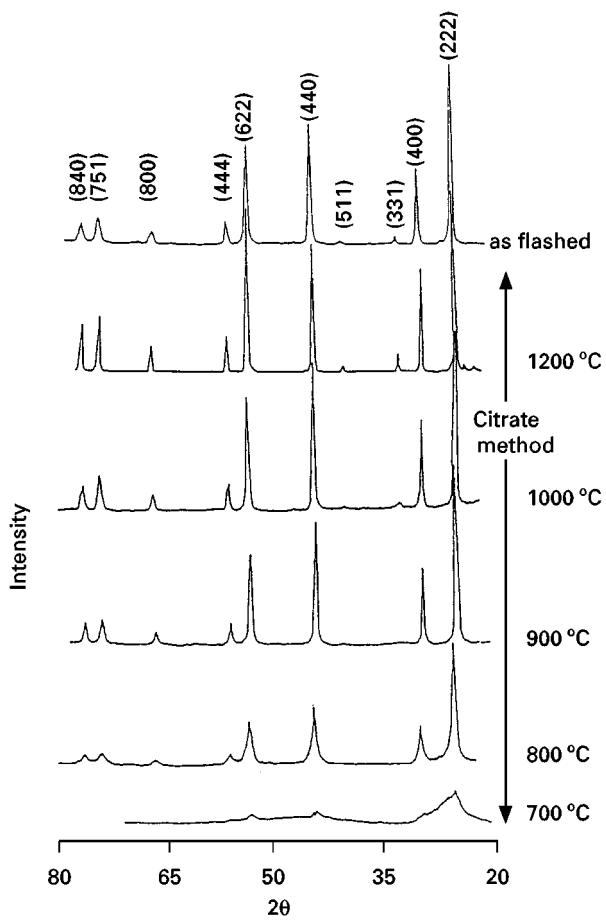

Figure 5 XRD patterns of lanthanum zirconate prepared through citrate route after heating at different temperatures and the sample prepared through flash decomposition technique.

treatment (FCT) together with those samples obtained by the citrate method but heated at different temperatures (between 700 and 1000 °C) are given in Fig. 5. The powder prepared by the citrate route and heated at 700 °C (CIT 700 °C) for 66 h shows the appearance of peaks corresponding to (2 2 2), (4 4 0) and (6 2 2) reflections of the pyrochlore phase. These peaks had very low intensities and were broad. After heating at 800 °C, the sample gave rise to additional peaks

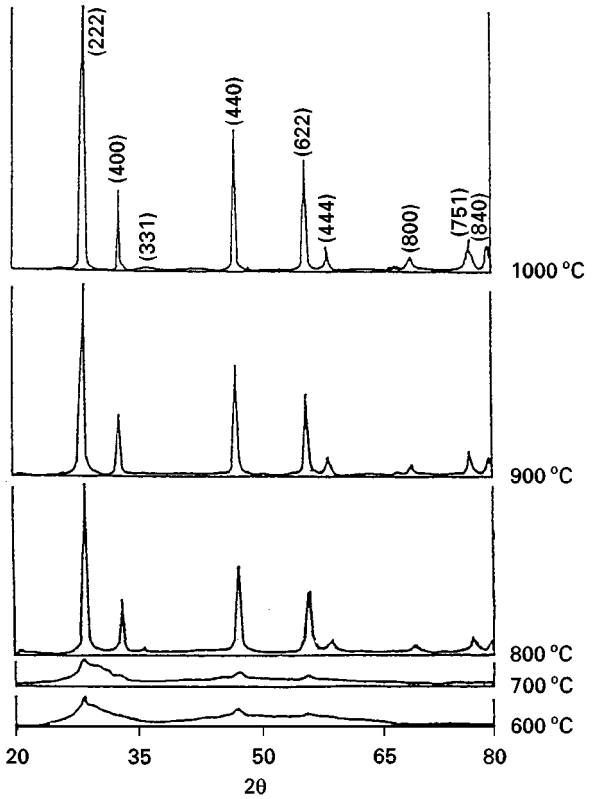

Figure 6 XRD patterns of lanthanum zirconate prepared through coprecipitation heated at different temperatures.

corresponding to the (4 0 0), (3 3 1), (8 0 0), (7 5 1) and (8 4 0) reflections of the pyrochlore structure [17]. As the temperature was increased further, the peaks became stronger and sharper, indicating that there was an improvement in the crystallinity of the lanthanum zirconate. All the main reflections corresponding to the lanthanum zirconate pyrochlore phase were present for samples heated at 900 °C (CIT 900 °C) or above [peaks corresponding to (2 2 2), (4 0 0), (3 3 1), (5 1 1), (4 4 0), (6 2 2), (4 4 4), (8 0 0), (7 5 1) and (8 4 0) reflections]. The "as-flashed powder" (FCT) gave an XRD pattern similar to that of the pyrochlore phase but with somewhat broader peaks than the citrate powder heated at 1200 °C (CIT 1200 °C).

The powder prepared through coprecipitation (CPT) was amorphous to X-rays as long as it was calcined below 600 °C. Fig. 6 shows the XRD of the gel which is heated at different temperatures. On heating to 600 °C (CPT 600 °C), reflections corresponding to the pyrochlore phase of $La_2Zr_2O_7$ [(2 2 2), (4 4 0) and (6 2 2)] were detected [17]. Further heated to temperatures above 600 °C gave rise to other reflections corresponding to $La_2Zr_2O_7$. With the increase in calcination temperature an increase in the intensity of the diffraction lines is observed, which in turn denotes an increased crystallinity.

Fig. 7 shows the Raman spectra of the lanthanum zirconate samples prepared by the flash combustion and citrate methods. Well defined Raman bands were not observed in the case of the citrate precursor heated to temperatures below 1000 °C. After calicination at 1200 °C, four of the six Raman bands [1] predicted for lanthanum zirconate were observed. The sharp band

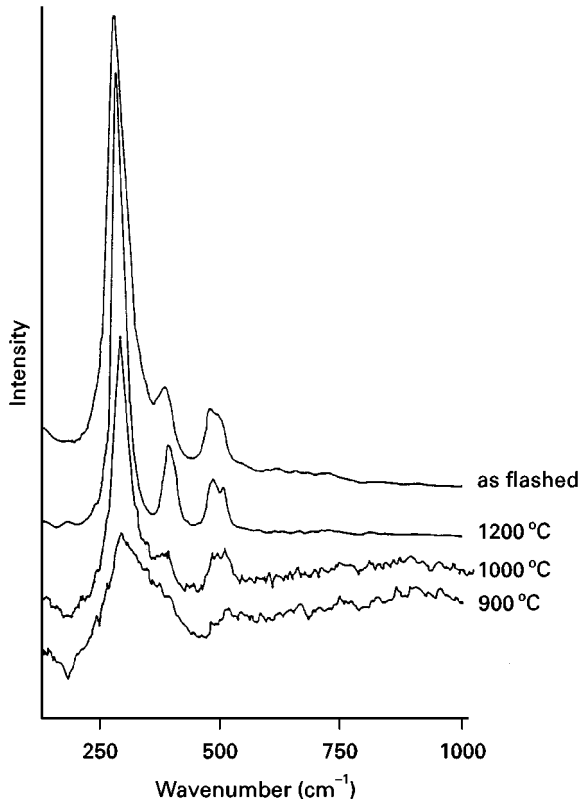

Figure 7 Raman spectra of lanthanum zirconate prepared through citrate route after heating at different temperatures and the sample prepared through flash decomposition technique.

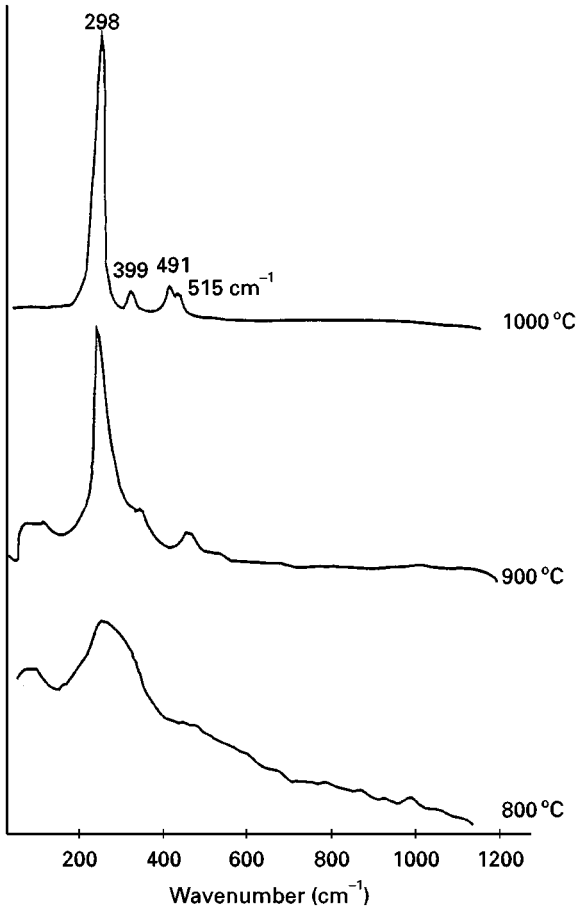

Figure 8 Raman spectra of lanthanum zirconate prepared through coprecipitation heated at different temperatures.

at 298 cm^{-1} can be assigned to an O–Zr–O bending vibration and the three bands at around 399, 491 and 515 cm^{-1} can be assigned to La–O and Zr–O stretching modes [18]. The optical modes, which have been reported to occur at 733 and 590 cm^{-1} [1], were not observed in this case. Michel *et al.* [18] have also failed to observe these bands. The Raman spectrum of the powder prepared by the combustion method (FCT) was similar to that of the one calcined at 1200 °C, which was prepared by the citrate route (CIT 1200 °C).

Fig. 8 shows Raman spectra of the coprecipitated lanthanum zirconate gel after calcination at different temperatures. Like the samples prepared by the citrate method, there is a gradual development of the crystalline phase on heating and the spectra are similar to those obtained by the citrate method.

Representation of nitrogen adsorption–desorption isotherms for samples of lanthanum zirconate prepared by the citrate and coprecipitation methods and calcined at 900 °C (CIT 900 °C and CPT 900 °C, respectively) are shown in Fig. 9. Fig. 9 also shows the isotherm for the sample prepared by flash combustion without further calcination (FCT). Isotherms are of type IV with hysteresis of type A, characteristic for a system with cylindrical pores [19]. The values of the surface area, calculated by applictaion of the Brunaver–Emmett–Teller (BET) equation, of the lanthanum zirconate prepared through different methods and heated at different temperatures for 4 h are shown in Fig. 10. With all the three preparation procedures, the area decreases with increasing calcination temperature. The surface area of the as-flashed powder (FCT)

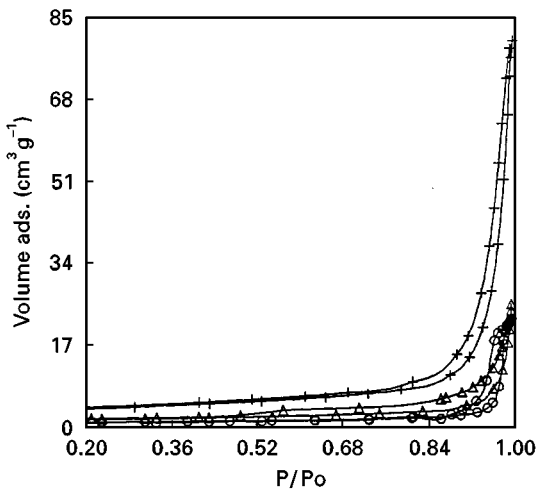

Figure 9 Adsorption/desorption isotherms of lanthanum zirconate prepared through (+) citrate and (○) coprecipitation routes after calcination at 900 °C and (△) as-flashed without calcination.

was found to be comparatively high (about 6 m^2 g^{-1}). This material experienced rapid reduction in surface area when heat treated at high temperatures and reached a value near zero after calcination at 1200 °C for 4 h. Even though the flash decomposition reaction proceeds at a very high temperature it is normally over within a few seconds. This implies that the powder prepared through the flash combustion technique has high reactivity. This may be the reason why this

TABLE I Range of surface area value ($m^2 g^{-1}$) of lanthanum zirconate prepared through different routes (calcination time, 4 h)

Temperature	Citrate method	Flash combustion method	Coprecipitation WW[a]	Coprecipitation EW[b]
1000	5.5–8.4	3.9–6.8	4.1–5.0	10–11
1100	2.3–5.5	2–4.6	2–3	7–7.6
1200	1–0.5	0	0	3.5–4

[a]WW, after precipitation-washed with water only.
[b]EW, after washing with water followed by ethanol.

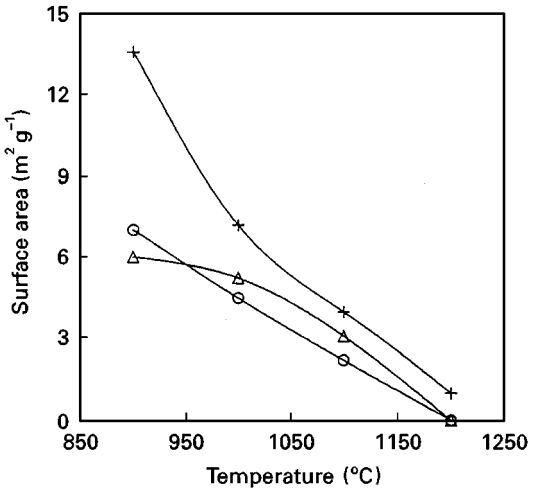

Figure 10 Surface area of lanthanum zirconate prepared through (+) citrate, (△) flash decomposition and (○) coprecipitation routes after calcination at different temperatures for 4 h.

material loses surface area rapidly on further heating. However, the powder obtained with the citrate method also loses surface area after heat treatment at high temperatures. The range of scatter is given in Table I. Data were obtained from three to five separate experiments, and two separate surface area measurements were carried out for each sample. The scatter is found to be less in the case of the sample prepared through coprecipitation compared with the other two cases. Table I also gives the surface area of the ethanol-washed (EW) coprecipitated sample heated at 1000, 1100 and 1200 °C. Lanthanum zirconate prepared through coprecipitation followed by ethanol washing has much higher surface area compared with the other methods.

From the above results coprecipitation is found to be a better way of preparing lanthanum zirconate in terms of reproducibility and maximizing surface area. Moreover, in the case of samples prepared through the citrate and flash combustion methods there are slight variations in the surface area for samples taken from different portions of the same batch.

Both citrate and flash combustion processes involve ignition and burning of the reacting mass. It is very difficult to control the process of burning. In practice, heat produced from the above processes is not dissipated uniformly over the whole mass. This is the most probable reason for the non-reproducibility of these methods. However, in the case of coprecipitation, the hydrolysis reactions can be controlled mainly by controlling the pH of precipitation and the rate of addition of the precursor.

4. Conclusions

1. Lanthanum zirconate prepared by the citrate and coprecipitation methods gives pyrochlore structure after heating above 900 °C, whereas the flash combustion technique gives the same phase without any additional heat treatment.

2. The flash decomposition technique gives a crystalline phase of lanthanum zirconate within a few minutes time and this has a surface area of about 6 $m^2 g^{-1}$. However, this decreases to a very low value on heating above 1100 °C.

3. Lanthanum zirconate prepared by the citrate route also loses surface area at higher temperatures; a value of 1.5 $m^2 g^{-1}$ was measured after calcination at 1200 °C.

4. Coprecipitation was found to give more reproducible results. Washing the resultant lanthanum zirconate gel with ethanol gave the highest surface area. Coprecipitation followed by ethanol washing is the preferred method for the preparation of high surface area lanthanum zirconate.

Acknowledgements

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