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Study of Solid State Reaction Involved in Synthesis of Nano Structured $Th_{0.9}Ce_{0.1}O_2$

C. ARORA CHUGH[1,2,*], A. BANTHIYA[2], DEEPIKA[2], D. BHARTI[2], G.A. RAMARAO[3] and Y.P. NAIK[3]

[1]Department of Chemistry, Lovely Professional University, Delhi-Jalandhar G.T. Road National Highway-1, Phagwara-144 402, India
[2]Department of Chemistry, Banasthali University, Banasthali-304 022, India
[3]Product Development Division, Radiochemistry and Isotope Group, Bhabha Atomic Research Centre, Mumbai-400 085, India

*Corresponding author: E-mail: charuarora77@gmail.com

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In the present paper, fuel for advanced heavy water reactor (AHWR) is simulated using thorium oxide with varying quantities of cerium oxide. Two mixed oxides were synthesized. GEL combustion technique was applied to attain oxides of thorium and cerium from their respective nitrate using citric acid as the gelating agent. The dried samples were characterized by IR and TGA studies. Intermediate and final products during TGA studies have been isolated and characterized by XRD studies. All the TGA runs during heating of thorium and cerium nitrate with citric acid dried Gels showed a two step process. The weight loss studies and the X-ray data of the product, helped in suggesting a possible mechanism. Kinetic study was carried out independently for each step. The reaction mechanism as observed during interactive procedure was diffusion controlled. The kinetic parameters (activation energy and pre-exponential factor) for each step in all reactions have been calculated. XRD studies show that with increase in cerium concentration in the oxides, the lattice parameter values have shown a decreasing trend for all the compositions studied. It was observed that in TGA studies with increase in cerium concentration, the final temperature of the reactions have shown a decreasing trend. Model fitting for the reaction suggested that the reaction obeyed Avrami-Erofeev solid diffusion controlled model represented by the kinetic equation:

$$k^*t = [-\ln (1-\alpha)]^{3/4}$$

The rate constant for this first step reaction was determined as function of temperature. A least square line could be fitted to the value of k obtained at different temperatures. It is observed that rate constant is related to temperature as per the equation:

$$\ln k = 51.23\text{-}82620.5/T \text{ (for first step)}$$

$$\ln k = 50.02\text{-}40079.2/T \text{ (for second step)}$$

SEM studies of the powders reveal that the synthesized oxides have a tendency to form agglomerate of varying size ranging from 50-100 μm in case of mixed oxides but the size of thorium oxide powder so synthesized have pore size 10-100 μm. SEM studies also reveal that each agglomerate contains approximately 10-100 individual particles.

Key Words: Oxides of thorium and cerium, GEL combustion technique.

INTRODUCTION

Nuclear energy has its importance as a sustainable energy resource for our country. India has nearly one third of the entire world's thorium, which is a fertile element and on irradiation in a nuclear reactor it captures a neutron to produce a valuable isotope of uranium, uranium-233 as per the reaction given below:

$$^{233}Th_{90} + {}^{1}n_0 \rightarrow {}^{233}Th \rightarrow {}^{233}Pa \rightarrow {}^{233}U$$

This can be used as a substitute to ^{235}U in nuclear reactor fuels.

One ton of thorium can produce nearly 1 GW of electricity for a year in an efficient thorium cycle reactor. Advanced heavy water reactor (AHWR) and accelerator driven sub-critical system (ADSS) are the two important technological milestones[1] for the third stage of nuclear power programme which envisages utilization of thorium and plutonium as a fuel. In the present work the fuel for the AHWR is simulated using thorium oxide with varying quantities of cerium oxide. Nano-structured homo-geneously mixed powdered mixtures of varying composition were synthesized using GEL entrapment of the metallic ions, followed by heat treatment[2-4].

EXPERIMENTAL

Preparation of dried GEL powder mixtures of Ce(IV)-Th(IV) citrate: Thorium cerium mixed oxide were synthesized by GEL entrapment technique taking cerium and thorium nitrate in various compositions as reported in Table-1 using SOL/GEL techniques. Citric acid has been used as the cheleting agent. Citrate ion acts as a chelating agent during drying process and does not allow any of the cations to precipitate

TABLE-1
PREPRATION OF CITRATE GEL MIXTURE CONTAINING VARYING COMPOSITION OF Ce(III) AND Th(IV) IN SOLUTION

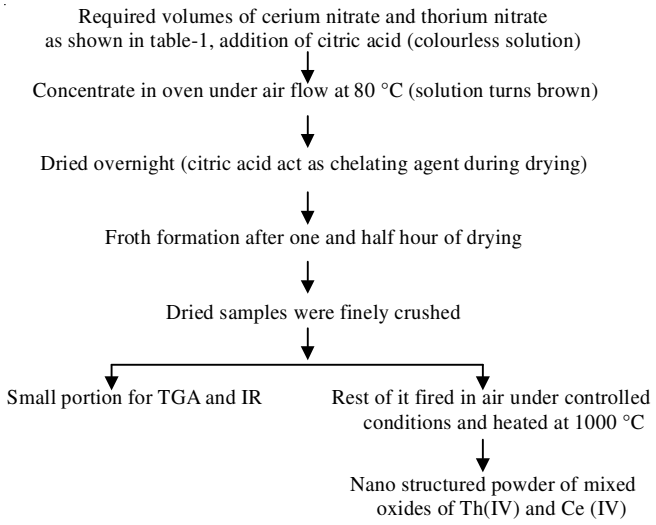
Sample no.	$Ce(NO_3)_3.6H_2O$ (mL)	$Th(NO_3)_4.4H_2O$ (mL)	Citric acid (mL)	Dried GEL power No	ThO_2-CeO_2 oxide sample no
1	0.00	5.00	5.00	S-1	$Th_1Ce_0O_2$
2	0.50	4.50	5.00	S-2	$Th_{0.9}Ce_{0.1}O_2$
3	2.50	2.50	5.00	S-3	$Th_{0.5}Ce0.5O_2$
4	5.00	0.00	5.00	S-4	$Th_0Ce_1O_2$

prematurely. The whole mass dries as a FOAMED GEL with cations uniformly distributed over the whole mass (random distribution) statistically.

The hydrolysis reactions are as follows:

$$Ce(NO_3)_3 + H_2O \rightarrow Ce(OH)_3 + 3HNO_3$$
$$Th(NO_3)_4 + 4H_2O \rightarrow Th(OH)_4 + 4HNO_3$$
$$2HNO_3 \rightarrow H_2O + 2NO_2 + 1/2O_2$$

TGA was chosen for the present study to predict the mechanism of the GEL combustion and to find the combustion temperature. Calcium oxalate mono hydrate supplied by NIST as a standard reference material was used for the calibration. Method of preparation has been shown in flow chart-1.



Flow Chart-1

Characterization of nano structured powered was done by XRD (Fig. 1) and SEM studies.

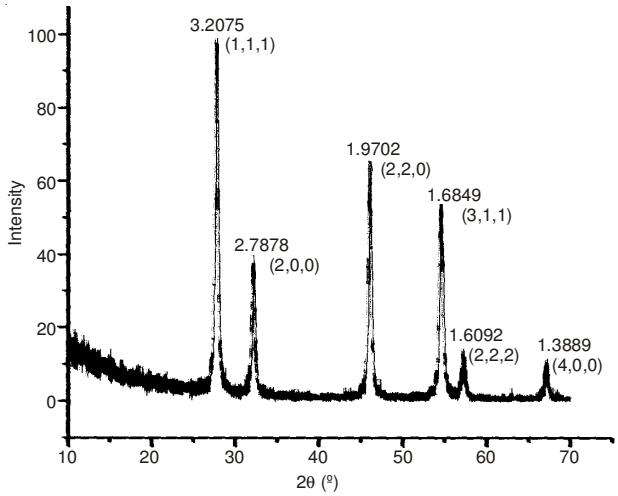


Fig. 1. XRD spectra of the final product $Th_{0.9}Ce_{0.1}O_2$ obtained after TGA run of sample

RESULTS AND DISCUSSION

Figs. 2 and 3 show the TGA curves for the sample $Th_{0.5}Ce_{0.5}O_2$ and $Th_{0.9}Ce_{0.1}O_2$. The absence of any mass loss step near 373 K indicates that the water of hydration has been lost during the drying process. It is also clear from the TGA curve that the reaction of the GEL mixture takes place in two steps. In the first step formation of hydroxyl thorium cerium citrate with the evaluation of oxides of nitrate, CO_2 and water vapour takes place. The mass losses during the first step in TGA curve is gradual and slow, whereas the DTA curve reveals a pattern showing two exothermic peaks giving information regarding the enthalpy change taking place in two different steps involving the reaction of hydroxyl cerium nitrate with citric acid followed by the reaction of hydroxyl thorium nitrate.

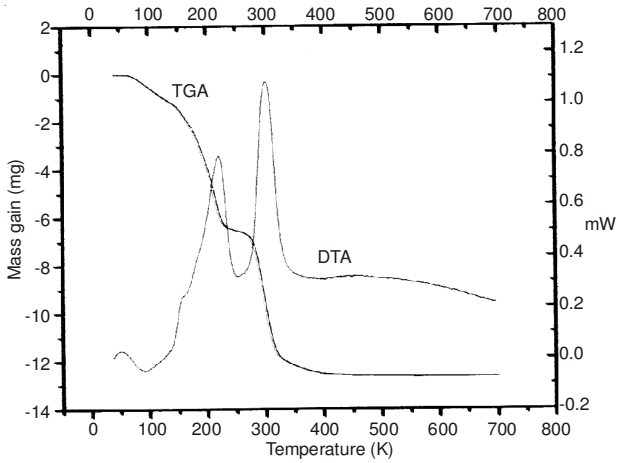


Fig. 2. TGA/DTA curve for sample $Th_{0.5}Ce_{0.5}O_2$ obtained at a heating rate of 5 K/min and dry air flow of 30 mL/min

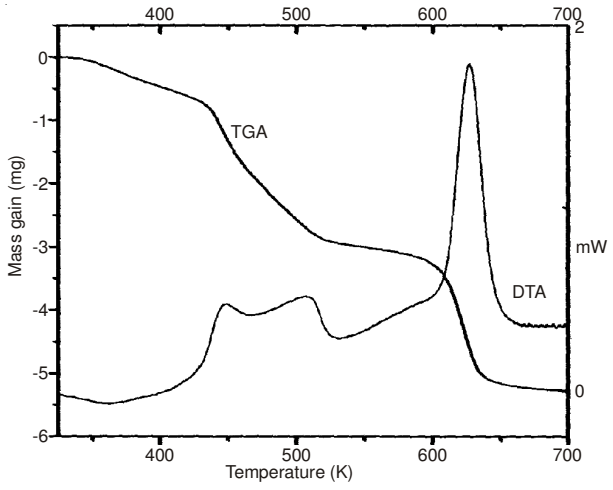


Fig. 3. TGA/DTA curve for sample $Th_{0.9}Ce_{0.9}O_2$ obtained at a heating rate of 5 K/min and dry air flow of 30 mL/min

TABLE-2
ACTIVATION ENERGY, PRE EXPONENTIAL FACTOR AND EXPRESSION FOR RATE CONSTANTS FOR VARIOUS STEPS OF THERMAL DECOMPOSITION OF Th : Ce MIXED OXIDE SAMPLES

Sample	Step	Activation energy (KJ/mol)	Pre exponential factor	Rate constant
$Th_1Ce_0O_2$	1st	77.5	1.53×10^6	ln k = 25.764-25603.0/T
	2nd	211.0	3.38×10^{15}	ln k = 33.02125-26003.48/T
$Th_0Ce_1O_2$	1st	32.4	14.30	ln k = 1.14002-4273.20/T
	2nd	71.9	9.89×10^3	ln k = 7.20971-9162.08/T
$Th_{0.5}Ce_{0.5}O_2$	1st	128.1	8.701×10^{12}	ln k = 27.20471-15857.89/T
	2nd	114.2	2.828×10^7	ln k = 14.8141-14293.32/T
$Th_{09}Ce_{0.1}O_2$	1st	703.3	3.395×10^7	ln k = 151.23-82620.5/T
	2nd	333.3	3.375×10^{23}	ln k = 50.02-40079.2/T

In the second step the oxidative decomposition of hydroxyl thorium cerium citrate to thorium cerium oxide takes place. It is clear from TGA curve that the rate of reaction is slow as a result of witch magnitude of this step in the TGA is high due to gradual mass loss.

Kinetic parameters and variation of lattice parameter with cerium content has been reported in Tables 2 and 3 respectively.

TABLE-3
VARIATION OF LATTICE PARAMETER 'a' WITH Ce CONTENT

Compound	$Th_{09}Ce_{0.1}O_2$	$Th_{0.5}Ce_{0.5}O_2$	$Th_0Ce_1O_2$	$Th_1Ce_0O_2$
a (Å) value	5.65	5.40	5.40	5.30

Conclusion

The purpose of this project was to find out the optimum condition for preparation of thorium cerium mixed oxide powder by a GEL combustion technique with subsequent calcination at different temperature and time in air. The GEL combustion technique was found to have several advantages over solid state reaction route, such as, ease of control, stoichiometry, submicron size particles and good homogeneity. GEL combustion technique was applied to attain oxides of thorium and cerium from their respective nitrate solution using citric acid as the gelating agent. The dried samples were characterized by IR and TGA studies. Intermediates and final products during TGA studies have been isolated and characterized by XRD studies.

All the TGA runs during the heating of thorium and cerium nitrate with citric acid dried GELs showed a two step process following Avrami -Eroveef diffusion control solid state reaction mechanism. The weight loss at each step and the X-ray data of the product at each step, helped in arriving at a possible reaction. It was observed from the XRD studies that with increase in cerium concentration in the oxides, the lattice parameter values have shown a decreasing trend for all the five compositions studied. It was observed in TGA studies that with increase in cerium concentration, the final temperature of the reactions have shown a decreasing trend. Kinetic analysis was carried out independently for each step and kinetic data have been derived. Since in burning of the organic moiety with compounds yielded gaseous products. The reaction mechanism as observed during interactive procedure was diffusion controlled. The kinetic parameters such as Activation energy and pre-exponential factor for each step in all the reactions have been tabulated.

SEM studies of the powders reveal that synthesized powder have a tendency to form agglomerate of varying size ranging from 50-100 m in case of mixed oxides but the size of thorium oxide powder so synthesized is having 10-50 μm SEM studies also reveal that each agglomerate contains approximately 10-100 individual nano particles.

These studies may lead to synthesis of nanostructured sustainable fuels for new generation nuclear power reactors.

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