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A facile and novel route to high surface area ceria-based nanopowders by salt-assisted solution combustion synthesis

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Abstract

A novel salt-assisted combustion process to synthesize high surface area ceria-based nanopowders has been developed. The effects of fuel-to-oxidant ratios, type and amount of added salt on the characteristics of the resultants were investigated by powder X-ray diffractometry (XRD), transmission electron microscopy (TEM) and BET surface area analysis. The facile addition of soluble inert salt in the redox mixture solution for combustion synthesis was found to result in the formation of well-dispersed nanoparticles and a drastic increase of specific surface area from 14.10 to 156.74 m^2/g. Finally, a mechanism scheme was proposed to illustrate the possible formation processes of highly dispersed nanoparticles.

Keywords: Salt-assisted; Solution combustion synthesis; Ceria-based nanopowders; Ethylene glycol; High surface area

1. Introduction

Ceria and ceria-based nanopowders have a wide range of applications, for example, solid electrolytes for SOFC [1], automotive three way catalysts [2], petroleum-cracking catalyst [3], oxygen sensors [4], chemical–mechanical polishing [5], and UV filter [6].

In recent years, since high surface area ceria nanoparticles show superior physical and chemical properties to bulk particles, much effort has been focused on increasing specific surface area and decreasing the grain size into nanometer range to enhance catalytic activity, sinterability, and other properties [7]. Ceria-based nanopowders have been reported to be synthesized by different techniques including hydrothermal [8], mechanochemical [9], sonochemical [10], precipitation [11], sol–gel [12], spray-pyrolysis [13], and microemulsion [14], etc.

Among the available chemical processes, self-sustaining solution combustion synthesis is convenient in process, simple in experimental device and saving in time and energy consumption in comparison to the above-outlined techniques [8–14]. Therefore, many attempts have been devoted to synthesis of ceria-based nanopowders via a solution combustion synthesis route. In the conventional solution combustion synthesis process, the properties of the product like crystallite size, specific surface area, morphology, phase, degree and nature (hard or soft) of agglomeration are usually controlled by choosing fuel and adjusting fuel-to-oxidant ratio. So far, ceria-based nanopowders have been synthesized by a combustion synthesis process using various fuels, such as glycine [15], citric acid [16], urea [17], oxalyldihydrazide [18], carbohydrazide [18], etc. In our previous work, ethylene glycol was firstly used as a fuel to synthesize nanocrystalline ceria-based powders [19]. Recently, a novel microwave-induced combustion technique has been employed in the synthesis of ceria-based nanopowders [20]. Although the combustion-synthesized powders have higher surface areas than the powders prepared by conventional solid-state methods [21], all the above-mentioned ceria-based powders do not show desirably high surface areas corresponding to their rather small crystallite sizes due to the inseparable agglomeration of nanocrystallites [15–20]. Hence, synthesis of high surface area well-dispersed nanoparticles has been a challenging issue in the solution combustion synthesis.

In this paper we report a novel approach for the combustion synthesis of high surface area ceria-based nanoparticles via facile introduction of inert soluble salt into the redox mixture solution. It was found that salt inclusion breaks up the three-dimensional porous structure, typical of the combustion-synthesized resultants and greatly enhances specific surface

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area. Moreover, acting as agglomeration inhibitor and inorganic template, salt is cheap compared with organic template, readily soluble in water, thermally stable to high temperature, easily removed from the as-prepared product mixture and finally recyclable.

2. Experimental procedure

$Ce(NO_3)_3{\cdot}6H_2O$ (99.5%), $Sm(NO_3)_3{\cdot}6H_2O$ (99.9%), $Gd(NO_3)_3{\cdot}6H_2O$ (99.9%), ethylene glycol (99%), NaCl (99.9%), KCl (99.9%), $CaCl_2$ (99.9%) and LiCl (99.9%) were used as received. According to the stoichiometric ratios of $Ce_{0.75}RE_{0.25}O_2$ (RE = Ce, Sm or Gd), the required ethylene glycol–nitrate molar ratios and the amount of added salt, the proper amount of cerium nitrate, samarium nitrate (gadolinium nitrate) when required, ethylene glycol and salt were dissolved in a minimum volume of deionized water in a quartz beaker to obtain transparent solution and evaporated on a hot plate adjusted at 110 °C. At this stage, the viscous liquids swelled, followed by the evolution of a large volume of gases, then self-propagating solution combustion occurred, yielding loose light yellow powder. In order to remove salt, as-burnt powders were boiled in deioned water, filtered and washed with deionized water and ethanol. Finally, the product was dried in an oven at 80 °C for 2 h.

Phase identification via X-ray diffractometry (XRD) was performed on a Bruker Advance D8 X-ray diffractometer using Cu Kα radiation. The crystallite size was calculated from line broadening of the (1 1 1) XRD peak by Scherrer's formula. Transmission electron microscopy (TEM) was carried out with a JEOL TEM-200CX microscope. The TEM particle size D_{TEM} was average value determined by TEM observation. The specific surface area S_{BET} of the powders was measured with a COULTER SA 3100 analyzer using the multipoint BET adsorption technique. The particle size D_{BET} was estimated from the formula: $D_{BET} = 6000/\rho \times S_{BET}$, where ρ is the theoretical density of the powder [7.13, 7.21, and 7.18 g/cm^3 for CeO_2, $(Gd_2O_3)_{0.1}(CeO_2)_{1.8}$, and $(Sm_2O_3)_{0.1}(CeO_2)_{1.8}$, respectively], S_{BET} is the BET surface area value (m^2/g). The degree of agglomeration of the obtained particles was valuated via D_{BET}/D_{XRD}.

3. Results and discussion

In our previous work [19], we investigated combustion synthesis of nanocrystalline ceria-based powders employing ethylene glycol–nitrate as fuel-oxidant couple. The as-synthesized powders exhibit the typical morphology of porous fractal composed of tightly agglomerated nanocrystallites. Two-hour ball milling did not greatly enhance the specific surface areas. Many documents have revealed that the conventional solution combustion synthesis method often obtains nanophased rather than nanosized particles which are nanometer in crystallite size calculated by the Scherrer's formula [15,22]. As the nanocrystallites are agglomerated/sintered together and virtually inseparable, the obtained products do not show high specific surface areas corresponding to their small crystallite sizes. Recently, we found that the introduction of soluble salt into redox mixture solution can effectively prevent nanocrystallites from sintering and forming inseparable three-dimensional network agglomerates. We denote the method as salt-assisted solution combustion synthesis (SSCS) in comparison to conventional solution combustion synthesis (CSCS), i.e. salt-free solution combustion synthesis.

Based on the principle of propellant chemistry [23], assumed that in the case of ethylene glycol–nitrate combustion, primarily N_2, CO_2, and H_2O are evolved as the gaseous products, the salt-assisted redox combustion reaction to synthesize ceria can be generalized and expressed as follows:

$$\begin{aligned}&Ce(NO_3)_3{\cdot}6H_2O(c) + \psi HOCH_2CH_2OH(l)\\ &\quad + (5/2\psi - 7/2)O_2(g) + n\mathrm{SALT}(c)\\ &= CeO_2(c) + 3/2N_2(g) + 2\psi CO_2(g)\\ &\quad + (6 + 3\psi)H_2O(g) + n\mathrm{SALT}(c) \qquad (1)\end{aligned}$$

where (c) crystalline, (g) gas, (l) liquid, SALT: added salt.

In the present work, fuel-to-oxidant molar ratios (which is hereafter termed as $EG/NO_3{}^-$) and amount of added salt (which is hereafter expressed as the molar ratio of salt to metal ion, SALT/M for short) were varied systematically to investigate the effect of $EG/NO_3{}^-$ and SALT/M on characteristics of the as-prepared powders. It was established that the auto-propagating combustion reaction occurs for a limited range of fuel-to-oxidant molar ratio, depending upon the nature of the fuel and the amount of the added salt.

It is well known that the enthalpy of combustion can be expressed as

$$\Delta H^\circ = \sum (n \times \Delta H_f^\circ)_{\mathrm{products}} - \sum (n \times \Delta H_f^\circ)_{\mathrm{reactants}} \qquad (2)$$

where n is the molar number. Using the thermodynamic data for various reactants and products, the enthalpy of the reaction for Eq. (1) as a function of the ψ can be determined as follows [19]:

$$\Delta H^\circ\,(\mathrm{kcal}) = -122.14 - 252.65\psi \quad (\mathrm{at}\ 25\,^\circ\mathrm{C}) \qquad (3)$$

The following equation can be used to theoretically approximate the adiabatic temperature of the combustion reaction system.

$$Q = -\Delta H^\circ = n_{\mathrm{salt}}\,\Delta H_{\mathrm{m}} + \int_{298}^{T} \sum (n\,C_p)_{\mathrm{products+salt}}\,\mathrm{d}T \qquad (4)$$

where Q is the heat absorbed by the products and the added salt under adiabatic condition, n_{salt} and ΔH_{m} the molar number and the melting enthalpy of the added salt, respectively, T the adiabatic flame temperature of the combustion reaction system and C_p is the heat capacity of the products and salt at constant pressure. According to Eq. (3), when ψ is fixed, the enthalpy of reaction for Eq. (1) is certain. Referring to Eq. (4), it can be concluded that the adiabatic flame temperature in the absence of salt is higher than that in the presence of salt. In the combustion synthesis process, salt absorbs large reaction heat due to the temperature rising and melting of the added salt. Hence, the adiabatic flame temperature of the reaction system can be also adjusted by adding different amount of different salt besides by altering fuel-oxidant molar ratio, which provides an alternative