

Preparation, characterization and catalytic performance of $\text{SrTi}_{0.9}\text{Li}_{0.1}\text{O}_3$ ultrafine powders

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Abstract

$\text{SrTi}_{0.9}\text{Li}_{0.1}\text{O}_3$ ultra-fine perovskite oxide powders were prepared by the ultrasonic spray pyrolysis technique and sol–gel method, respectively. We investigated the physical properties (i.e. crystalline phase and the microstructure) of the prepared powders using XRD, PSD, SEM and TEM techniques and also evaluated the catalytic performance of the resulting powders to the oxidative coupling of methane (OCM). By adding NH_4NO_3 into the precursor solution, uniform, solid and spherical $\text{SrTi}_{0.9}\text{Li}_{0.1}\text{O}_3$ particles with a diameter of around 500 nm and the single perovskite crystal phase can be obtained at 900 °C. The resulting $\text{SrTi}_{0.9}\text{Li}_{0.1}\text{O}_3$ ultrafine powder prepared by the spray pyrolysis exhibited a much better catalytic performance (higher C_2 selectivity and C_2 yield) to OCM than that prepared by the sol–gel method.

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1. Introduction

Some perovskite oxides such as $\text{SrTi}_{1-x}\text{Li}_x\text{O}_3$ possess good catalytic performances for methane oxidation, and thus they can be used as the anode material for direct methane solid oxide fuel cells (SOFCs) or as the catalyst for oxidative coupling of methane (OCM) [1–3]. Such composite oxide materials can be synthesized through the solid-state reaction, co-precipitation, sol–gel or the spray pyrolysis method [4–7]. Depending on the formation routes, physical properties of the oxide powders like microstructure, surface area, particle size distribution, or homogeneity of the metal ion distribution are quite different and therefore their practical performance differs accordingly. Among the powder preparation techniques, spray pyrolysis which involves the preliminary formation of minute droplets from the mixed solution containing stoichiometric metal ions and the subsequent hot pyrolysis, attracts increasingly considerable attention in the synthesis of complex materials, due to its low cost, simple and fast characteristics [8–11]. However, because of

the rapid evaporation of the solvent on the surface of the droplet, hollow or dented spherical particles [12] are often produced, leading to irregular powder morphology and low utility efficiency. Later, this method was modified by the introduction of NH_3 during pyrolysis to prevent the formation of hollow particles [13,14]. However, the droplets with concentrated solution of nitrate will react with NH_3 to form a pliable continuous skin on the surface of each droplet, which is easily collapsed to form larger particles with irregular shapes. In this work, we improved this ultrasonic spray pyrolysis technology by adding NH_4NO_3 into the precursor solution as a promoter to prepare solid and ultrafine catalyst particles for methane oxidative coupling reaction. We investigated the effects of NH_4NO_3 addition on the morphology and crystal phase of the formed powders, and evaluated the catalytic performance of ultrafine $\text{SrTi}_{0.9}\text{Li}_{0.1}\text{O}_3$ particles for the OCM reaction.

2. Experimental

2.1. Sample preparation

Fifteen milliliter tetrabutyl titanate was dissolved in 50 ml of 0.1 M nitric acid. The clean layer in the beaker bottom was transferred to another vessel using a separatory funnel.

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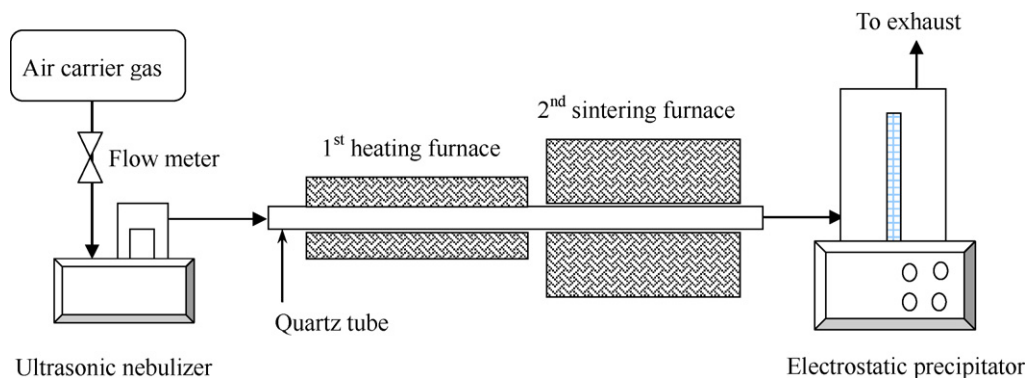


Fig. 1. Schematic diagram of the ultrasonic spray pyrolysis setup.

Stoichiometric amounts of strontium and lithium nitrates were dissolved in the above separated clean solution to get a precursor solution with the metal ion concentration of 0.2 mol/L. A certain amount of NH_4NO_3 was added into the precursor solution to a ratio of metal ion and NH_4NO_3 of 1:1. A schematic of the spray pyrolysis rig is illustrated in Fig. 1. The prepared precursor solution was injected into the ultrasonic sprayer (1.6 MHz frequency) and the air-flow rate was maintained at $0.2 \text{ m}^3/\text{h}$. The first temperature zone was adjusted to 300°C to preheat the solution and remove moisture in the droplet for better pyrolysis for subsequent processes at a temperature range of $600\text{--}900^\circ\text{C}$. The resulting particles were collected by an electrostatic collector and the exit gas was discharged into the well-ventilated fume hood.

The synthesis procedure of $\text{SrTi}_{0.9}\text{Li}_{0.1}\text{O}_3$ particles using the sol-gel method is briefly described below. The required stoichiometric amount of strontium nitrate and lithium nitrate were dissolved in the distilled water. Tetrabutyl titanate was added dropwise into the solution with certain amount of nitric acid as the chelating agent. The mixture was stirred at $70\text{--}80^\circ\text{C}$ until the transparent gel was formed. The gel was burned under continuous heating and the residues after burning were ground into powder which was heated for 2 h at 900°C for structure characterization and catalytic performance test.

2.2. Characterization techniques

Structural phases were determined for sintered powders in a Bruker (D8 Advance) diffractometer using Cu K_α radiation. A continuous scan mode was used to collect 2θ data from 10° to 90° with a 0.02 sampling pitch and a $2^\circ/\text{min}$ scan rate. X-ray tube voltage and current were set at 35 kV and 30 mA. Morphologies of the sintered samples were observed using a Scanning Electron Microscopy (FEI Sinrion 2000, Netherlands) and Transmission Electron Microscopy (HITACHI 800, Japan). A laser particle size distribution analyser (Winner 2000) was used to measure the particle size and particle size distribution of the resulting powders.

2.3. Catalytic performance test

A self-assembled quartz fixed bed reactor was used to evaluate the catalytic performance of synthesized materials.

0.5 g catalyst was loaded into the center part of the quartz reactor with a length of 25 cm and inner diameter of 0.6 cm. Both ends of the quartz tube were loaded with inert alumina spheres (200 mesh). The catalyst was activated by oxygen flow at 600°C for 1 h before reaction. The mixture of oxygen, methane, and helium was introduced into the reactor and the flow rate was controlled by mass flow controller (D08-8B/ZM) and calibrated using a soap bubble flowmeter. The product was analyzed after 1 h of reaction. Fig. 2 illustrates the scheme of catalytic performance test.

The effluent gas composition was analyzed using a gas chromatograph (Agilent 6890N), which was equipped with a thermal conductivity detector and a 3 m-long column loaded with the carbon molecular sieve Carbosieve S-II. High purity helium (purity $> 99.95\%$) was used as the carrier gas with a flow rate of $30 \text{ cm}^3/\text{min}$. The methane conversion (X_{CH_4}), C_2 selectivity (S_i) and C_2 yield (Y_{C_2}) were calculated as follows according to the gas composition before and after reaction:

$$X_{\text{CH}_4} = \left(1 - \frac{F_{\text{out}}x_{\text{CH}_4}}{F_{\text{in}}y_f} \right) \times 100\% \quad (1)$$

$$S_{\text{C}_2} = \frac{2F_{\text{out}}x_{\text{C}_2}}{F_{\text{in}}y_f - F_{\text{out}}x_{\text{CH}_4}} \times 100\% \quad (2)$$

$$Y_{\text{C}_2} = X_{\text{CH}_4} \times S_{\text{C}_2} \quad (3)$$

where y_f , x_{CH_4} are the methane contents before and after reaction, respectively. F_{in} , F_{out} are the flow rates of feed in and feed out, respectively.

3. Results and discussion

3.1. Thermal evolution to $\text{SrTi}_{0.9}\text{Li}_{0.1}\text{O}_3$ perovskite

Fig. 3 describes the X-ray diffraction patterns of $\text{SrTi}_{0.9}\text{Li}_{0.1}\text{O}_3$ powder synthesized at different conditions. Fig. 3a–d illustrates the crystal development of $\text{SrTi}_{0.9}\text{Li}_{0.1}\text{O}_3$ powder prepared from spray pyrolysis without addition of NH_4NO_3 . Powders calcined at 600 and 700°C were composed of $\text{Sr}(\text{NO}_3)_2$ and perovskite $\text{SrTi}_{0.9}\text{Li}_{0.1}\text{O}_3$. When the calcination temperature was increased to 800 and 900°C , the XRD patterns displayed the co-existence of TiO_2 and $\text{SrTi}_{0.9}$.

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