



Synthesis of uniformly porous NiO/ZrO₂ particles

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ABSTRACT

Porous NiO–ZrO₂ particles were successfully synthesized using a spray-drying method with polystyrene latex (PSL: 400 nm) as a template and starting materials that included NiO powder (7 nm) and ZrO₂ sol (1.2 nm). Porous particles with an average diameter of 4.5 μm and nearly spherical, narrow pores with an average size of ~300 nm were obtained from the precursor at a pH of 3.7. The Brunauer, Emmett and Teller (BET) surface area of the prepared particles was relatively high—about 27 m²/g. When the solution pH was increased to 9.7, the particle morphology became completely spherical, indicating that the morphology of prepared particles can be controlled by adjusting the pH. Calcinations at 900 and 1200 °C were carried out to estimate the thermal stability of the prepared particles, which had shrinkage of less than 36%. The existence of these pores means that various applications, such as electrodes and catalysts, will be possible for the prepared particles.

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1. Introduction

Nickel oxide (NiO) has attracted wide attention due to its promise for important applications such as electrodes, catalysts, electrochromic films, electrochemical supercapacitors, magnetic materials, and gas sensors [1–4]. Some distinctive properties of NiO, such as its abundance, and high electrical conductivity for fuel cell applications have been reported [1,5]. However, problems persist for the application of NiO: carbon deposition, sintering and deactivation at high temperatures, particularly in fuel cell applications. Various supports (such as Al₂O₃, SiO₂, TiO₂, CeO₂, ZrO₂, MgO, CaO, BaO) and promoters have been studied comprehensively in order to improve the activity and stability of nickel-based catalysts [3,6].

Zirconia (ZrO₂) was found to be one of the most effective materials to improve both the activity and stability of nickel-based catalysts [3,6]. ZrO₂ plays a crucial role in applications including optics, catalysis, adsorption, catalytic support, electrodes, and thermal barrier coating and sensors [7–9]. ZrO₂ is often included in composite systems, either as a promoter or as a supporter. ZrO₂ addition to a metal-supported catalyst can induce long-term stability [10,11]. Therefore, the addition of ZrO₂ particles to a nickel anode is able to take the thermal expansion coefficient mismatch between nickel and ZrO₂ [12]. The interaction between NiO and

ZrO₂ protects composites from sintering [13], thus, composites show great promise for applications involving high-temperature devices such as electrodes in fuel cells [12], sensors [14], and catalysts [15,16].

In order to enhance the performance of the composite particles, either as electrodes or as catalysts, composite particles are expected to have sufficient porosity to allow efficient fluid transport and to increase the active surface area for catalytic reactions [7,12,17]. Particles with small pores result in the poor diffusion efficiency of reactants and products in an intra-particle structure. However, while showing improved inside-pore diffusion efficiency, particles with large pore sizes usually have a small specific surface area [18]. Therefore, it is a significant challenge to synthesize particles containing pore sizes on the order of 300 nm. This pore size is the most suitable for efficient fluid transport due to its ability to prevent the pores from collapsing at high temperature and to prevent the descent of particles to the surface area. Generally, in the case of electrode materials, pore formers have been added to increase electrode porosity and decrease the overpotential [2]. Since the discovery of ordered mesoporous materials of the M41S family by the Mobil Corporation in 1992, templating methods have become widely used for the synthesis of a well-controlled structure of porous materials [19,20]. The advantage of the template method is that the morphology and size of the pores are set by the morphology and size of the template, and can therefore be designed and tailored easily, with both the final porosity and the surface area determined by the size of the template particles [7]. The most commonly used templates

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include silica spheres, polystyrene lattices, copolymer latexes and surfactants [21]. In the present work, the preparation of porous NiO–ZrO₂ was done using polystyrene latex (PSL) as a template.

Our group has successfully prepared various porous particles such as silica and brookite TiO₂ using a spray-drying method [22,23]. The spray drying method is fast, which can be scaled-up, continuous in process, low cost, generally environmentally friendly, and high-yield production of powder. Spray drying also maintains the stability of the powder flow during its process [24]. Particle morphology can also be controlled using this method. For instance, the prepared particle size can be adjusted by controlling the droplet size. An extensive review of spray-drying was given by Senatore et al. [25]. The explanation above shows that porous particles are relatively easier to handle. However, no detailed information regarding the synthesis of NiO–ZrO₂ porous particles has been yet reported in the previous literature.

The aim of the present study was to introduce a spray-drying method for the preparation of open pores of NiO–ZrO₂ composite particles with a controlled morphology and a high surface area. A detailed study of the controlling morphology of the porous NiO–ZrO₂ particles by adjusting the preparation conditions such as pH of solution, size of template particles, flow rate, temperature, etc., was the main objective of this research. We were able to control the size of the pores by determining the size of the template particles. The main product of this work which was open pores and particles with isolated pores were analyzed and compared based on the pH and zeta potential. In addition, the thermal stability of the prepared particles was investigated systematically.

2. Experimental

Porous NiO–ZrO₂ particles were made from a mixed precursor of NiO powder (7 nm, Noritake Co., Ltd., Japan) and colloidal ZrO₂ (1.2 nm, Sakai Chemical Co., Ltd., Japan) using PSL (~400 nm) as a template. The precursor, with a concentration of 1 wt%, was prepared by diluting NiO powder and as-prepared ZrO₂ sol into pure water. Both precursors were then mixed with a fixed composition of a 3:2 mass ratio for NiO/ZrO₂. PSL 400 nm in size at 9.5 wt% was then added to the composite mixed precursor. The mass ratio of NiO + ZrO₂:PSL was designed to be 2:7.5. Typically, spray drying has been accomplished using a two-fluid nozzle method (BÜCHI mini spray dryer B-290), which is shown schematically in Fig. 1. To obtain porous particles, the previous composite particles were reheated in an electric furnace (KDF 1700, Denken Co., Ltd.) in order to evaporate the PSL. Three different temperatures were used in this process step: 600, 900 and 1200 °C.

The solution pH was adjusted using the acid–base titration method. Nitric acid solution (1 N, Kanto Chemical Co., Inc.) was added to decrease the precursor pH to 1.5. An ammonia solution (28–30%, Kanto Chemical Co., Inc.) was used to increase the precursor pH, and the pH was adjusted to 5.7, 7.7 and 9.7. All of these pH measurements were carried out by pH meter (Piccolo).

Zeta potential measurement was carried out using a Malvern ZS NanoS analyzer (Malvern Instrument Inc., London, U.K.). The morphology of NiO–ZrO₂ was examined using scanning electron microscopy (SEM) (S-5000, Hitachi Ltd., Tokyo, Japan) and Transmission Electron Microscopy (JEOL-JEM-2010, 200 kV). The surface area was determined quantitatively using nitrogen adsorption by the Brunauer, Emmett, and Teller (BET) method at a relative pressure below 0.3 (monolayer adsorption). X-ray diffraction (XRD, Rigaku Denki RINT2000, Cu-K α , 20–80° (2 θ)) analysis was used to obtain information on the diffraction model

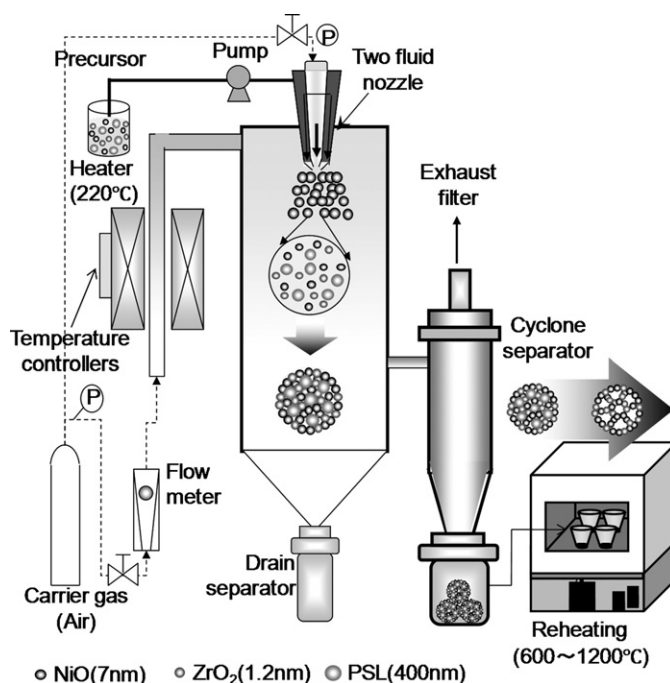


Fig. 1. Schematic diagram of the experimental setup of the spray-drying method.

and the particle crystallography. In addition, to determine the temperature of the PSL removal, thermogravimetric–differential thermal analysis (TG–DTA, TG–DTA 6200, Seiko Instrument Inc., Tokyo, Japan) was performed.

3. Results and discussion

3.1. Thermogravimetric (TG) analysis

TG–DTA characterization determines the removal temperature of PSL. Fig. 2 shows that the weight of PSL decreases drastically from 300 to 400 °C and then slopes slightly closer to 0 wt% at 400 °C onwards. This result implies that PSL starts decomposing at that temperature, and almost no PSL remains at temperatures higher than 400 °C. The weight of ZrO₂ starts decreasing slightly at 320 °C and then becomes constant at 450 °C onwards. The decreasing weight of ZrO₂ at the temperature up to 450 °C is

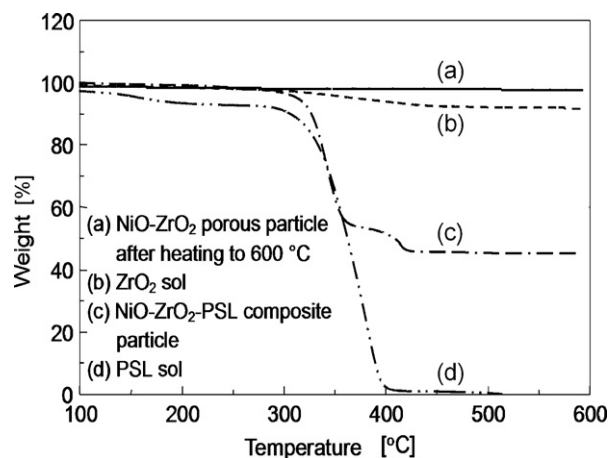


Fig. 2. TG–DTA curves of: (a) NiO–ZrO₂ porous particle after heating to 600 °C, (b) ZrO₂ sol, (c) NiO–ZrO₂–PSL composite particle, and (d) PSL sol.

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