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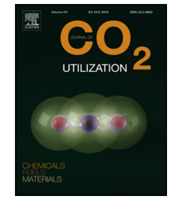

A core-shell structured $Fe_2O_3/ZrO_2@ZrO_2$ nanomaterial with enhanced redox activity and stability for CO_2 conversion

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ABSTRACT

A novel $Fe_2O_3/ZrO_2@ZrO_2$ nanomaterial with core-shell structure is proposed, where first Fe_2O_3 nanoparticles are loaded onto a ZrO_2 support as a core and afterwards the core is coated with a thin and porous layer of ZrO_2. Such combination of nanocoating and impregnation methods has been applied to synthesize core-shell oxygen storage nanomaterials with different iron oxide loading. 2D in-situ XRD patterns recorded during isothermal redox cycles at different temperatures (550–650 °C) show the evolution of Fe_3O_4 to metallic iron in $Fe_2O_3/ZrO_2@ZrO_2$ as a function of temperature. A detailed characterization of fresh and spent samples demonstrates that the $Fe_2O_3/ZrO_2@ZrO_2$ materials exhibit excellent structural stability (stable pore structure, specific surface area and core-shell morphology) and strong capability to resist sintering after 100 redox cycles at 650 °C for CO_2 conversion to CO compared to the samples prepared by impregnation only. The strong thermal stability of ZrO_2 coating materials contributes to keep up the activity of active phase during high-temperature environments.

1. Introduction

Carbon dioxide has become an attractive source of carbon for the chemical industry owing to its low cost and high availability. It is therefore of importance to establish efficient processes for converting CO_2 into chemicals. Chemical looping is such a process, originally a low-emission energy technology, with current application in production of chemicals, fuels, electricity, energy storage and with high potential in CO_2 utilization [1–9]. In a chemical looping process, a given reaction is divided into multiple subreactions, where oxygen storage materials (OSM) are reduced and regenerated in a cyclic fashion through the progress of the subreactions [10]. For example, if chemical looping is applied for CO_2 conversion to CO, the processing of a fuel is broken down into two, spatially or temporally separated half-steps: reduction of the oxygen storage material via reaction with the fuel and material re-oxidation with CO_2. This process utilizes more carbon dioxide than it produces in the reduction step [4,7,11–15], e.g. in the case of CH_4, the process can convert three times more CO_2 [15,16].

The key to success for chemical looping is the OSM which needs to show high redox properties, sufficient stability, low cost and environmental compatibility. Recently, large efforts have been focused on enhancing the performance of iron oxide as an effective OSM [17]. The latter include efforts to improve their redox properties, so as to achieve high stability during prolonged use, as pure iron oxide has a tendency towards sintering during redox cycling. The loss of surface area doesn't lead to a decrease of oxygen storage capacity but rather to a decrease in efficiency of the full process because reduction and re-oxidation time are increased [18,19]. In order to prevent iron oxide from sintering, a promoter such as Al_2O_3, MgO, SiO_2, CeO_2 and ZrO_2, is often used [4,20–26]. However, these promotors tend to form new phases like $AlFe_2O_4$, $MgFe_2O_4$, Fe_2SiO_4 and $CeFeO_3$ during the redox reactions. The overall OSM becomes less reactive in the presence of these phases, since the regeneration of the active iron oxides from the above mentioned iron spinels or perovskite requires much stronger reducing and oxidizing conditions. As a result, the oxygen storage capacity decreases significantly [11,23]. To avoid chemical interaction between the oxides of iron and the promoter material, ZrO_2 has received a great deal of attention owing to its inertness. Liu et al. conducted an extensive study on Fe_2O_3-ZrO_2 OSM for chemical looping, finding that the physical structure of ZrO_2 was

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relatively stable during cycling and no new phase formed [23]. The main method for synthesizing this material was co-precipitation, yielding a composite with uniformly distributed Fe_2O_3 and ZrO_2. However, sintering of the active material remains an issue, making it necessary to develop Fe_2O_3-ZrO_2 with a more stable structure.

Design of a core-shell structured material, a nanoparticle core coated with a stable shell, is a promising strategy to achieve this stability requirement [27–29]. A Fe_2O_3@ZrO_2 core-shell material with a nano-size core of active component and a thin shell of stable promoter is expected to show excellent reactivity and stability for chemical looping. Several studies have been performed to synthesize Fe_2O_3@ZrO_2 material via nanocoating of Fe_2O_3 with ZrO_2 in a hydrolysis process with a ZrO_2 precursor [30,31]. However, there are two challenges: (1) nanoparticles have a very high tendency to aggregate during the coating process, so multi-particle cores within the shell are usually formed [30]; (2) in general, the as-prepared Fe_2O_3 particle is non-densified, leading to an unstable support for the shell. It is common to see the core-shell structure collapse after high-temperature reaction. To avoid these drawbacks, here, a novel Fe_2O_3/ZrO_2@ZrO_2 nanomaterial with core-shell structure is proposed, where first Fe_2O_3 nanoparticles are loaded onto a ZrO_2 support as a core and afterwards the core is coated with a thin and porous layer of ZrO_2. The schematics of the synthesis pathway and the proposed core-shell material are illustrated in Fig. 1.

Using Fe_2O_3 nanoparticles supported on stable crystalline ZrO_2 as core material offers several advantages: the Fe_2O_3/ZrO_2 core not only eliminates the aggregation of nanoparticles during the coating process but also provides a densified and stable support for the shell. To protect the supported iron oxide particles from sintering under high-temperature environment, a ZrO_2 layer is deposited on the surface of the Fe_2O_3/ZrO_2 core by means of a general nanocoating process [32,33], in which P-123 (a nonionic amphiphilic surfactant) is used to create an active template layer on the core surface for shell formation. After the ZrO_2 layer synthesis, the P-123 is removed by calcination at 700 °C, leaving mesopores in the ZrO_2 shell, through which reduction and oxidation gases can reach the iron oxide. The size of the pores may be controlled by the temperature and time of the calcination treatment [34].

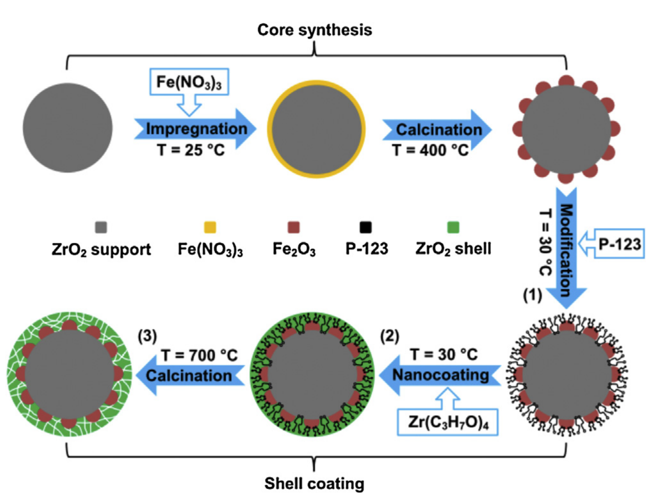

Fig. 1. Schematics of the proposed core-shell material and the synthesis pathway. The nanocoating strategy includes three steps: (1) the core material is activated by modifying its surface with a surfactant, (2) the active core acts as a template for shell deposition, typically a stable metal oxide MeO, by depositing a hydroxidic Me through hydrolysis of metal salts or alcoholysis of metal alkoxides, (3) afterwards a calcination procedure is applied to form a crystalline MeO shell as well as to remove the surfactant while leaving pores in the shell.

2. Experimental

2.1. Materials preparation

A ZrO_2 support was prepared by precipitation through addition of excess ammonium hydroxide. Typically, $ZrO(NO_3)_2{\cdot}6H_2O$ (18.76 g, Sigma-Aldrich, 99%) was added to de-ionized water (300 mL) under stirring. After 20 min, NH_4OH (10 mL, ACS reagent, 28.0–30.0% NH_3 basis) was added and the mixture was kept for 10 min under constant stirring. The precipitate was collected by filtration, washed with de-ionized water, dried at 120 °C for 4 h in an oven and calcined at 900 °C (with a heating ramp of 5 °C min^{-1}) for 2 h to form a stable crystalline phase.

The Fe_2O_3/ZrO_2 cores with 10 wt.% and 30 wt.% of Fe_2O_3 were prepared by incipient wetness impregnation using an aqueous solution containing the required amount of iron nitrate salt, $Fe(NO_3)_3{\cdot}9H_2O$ (Sigma-Aldrich, 99.99+%). The impregnated samples were kept overnight at room temperature, then dried at 120 °C for 4 h and calcined at 400 °C (with a heating ramp of 1 °C min^{-1}) for 1 h.

Fe_2O_3/ZrO_2@ZrO_2 OSM was synthesized by coating Fe_2O_3/ZrO_2 core material with a ZrO_2 nanoshell. Firstly, Fe_2O_3/ZrO_2 particles (1 g) were dispersed in absolute ethanol (150 mL) in a single neck flask. Then, the flask was sealed with a cork and heated to 30 °C under vigorous stirring. Afterward, P-123 (Sigma-Aldrich, average molecular weight ~5800) aqueous solution (1 mL, 4 wt.% in water) was added. After 1 h, zirconium propoxide solution (3.64 mL, Sigma-Aldrich, 70 wt.% in 1-propanol) was dropwise added into the flask in 5 min, and the coating process was allowed to proceed for 20 h at 30 °C. The product was collected by filtration, and the removal of organic compounds to form the porous ZrO_2 shell was achieved by a calcination step at 700 °C (with a heating ramp of 1 °C min^{-1}) for 1 h. In order to prove the protective effect of the ZrO_2 shell on the Fe_2O_3 particles during calcination and cycling reaction, another batch of 10 wt.% Fe_2O_3/ZrO_2 core material was calcined at 700 °C, i.e. the same temperature procedure as the Fe_2O_3/ZrO_2@ZrO_2 OSM for comparison. Core and core-shell materials are labelled as xFe/Zr and xFe/Zr@Zr, respectively, where x represents the Fe_2O_3 loading.

2.2. Characterization and measurements

The Brunauer-Emmett-Teller (BET) surface area of each sample was determined by N_2 adsorption at −196 °C (five point BET method using Gemini Micromeritics). The pore size distribution was calculated based on the classical Barrett-Joyner-Halenda (BJH) method using the Harkins and Jura Thickness Curve model. Prior to the measurements, the samples were outgassed at 200 °C for 2 h. The actual chemical compositions of as-prepared materials were determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICAP 6500, Thermo Scientific). The samples were mineralized by alkaline fusion with a mix of Li-tetraborate and Li-metaborate.

The crystallographic phases of fresh and spent materials were confirmed by ex-situ XRD measurements using a Siemens Diffractometer Kristalloflex D5000, with Cu Kα radiation. The powder patterns were collected in a 2θ range from 10° to 80° with a step of 0.02° and 30 s counting time per angle. By fitting of a Gaussian function to a diffraction peak, the crystallite size was determined from the peak width via the Scherrer equation, while the peak position gave information about the lattice spacing based on the Bragg law of diffraction [35].

Morphological and structural analyses were carried out using transmission electron microscopy (TEM)-based methods: scanning transmission bright field (STEM BF) and energy dispersive X-ray analysis (EDX). These techniques were implemented using a JEOL