



Short communication

Reverse water–gas shift reaction over ceria nanocube synthesized by hydrothermal method

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ABSTRACT

A well-defined ceria nanocube with six (100) planes was successfully prepared by a facile hydrothermal method. Hydrogenation tests on the carbon dioxide, and several advanced analysis techniques, were used to investigate the catalytic performance of ceria nanocube for reverse water–gas shift (RWGS) and understand the governing reaction mechanism. The results demonstrated that the obtained ceria was a typical mesoporous material with a fluorite structure, and mainly had cerium with +4 valence oxidation state. As-obtained ceria nanocube showed good performance for RWGS reaction, while nickel on ceria evidently promoted the hydrogenation of CO₂. An oxygen-transformation and metal-dissociation mechanism for RWGS reaction was proposed. The dissociation of carbon dioxide over ceria by directly oxidized oxygen vacancy was considered as a main reaction pathway of RWGS. Meanwhile, dissociated adsorption of CO₂ and hydrogen over nickel surface directly formed CO and supplied spillover hydrogen to nearby oxygen vacancies, respectively. The neighboring oxygen vacancies at the interface of nickel and ceria were considered as efficient active sites for CO₂ hydrogenation.

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1. Introduction

It is well known that carbon dioxide has a negative effect on the environment. It is furthermore the most abundant carbon source available. An interesting and attractive alternative to storing CO₂ through sequestration would be the recycling of the gas into energy-rich compounds [1]. Carbon dioxide hydrogenation through reverse water–gas shift (RWGS) forming syngas, which can form methanol or liquid hydrocarbons by a following Fisher-Tropsch synthesis, is considered to be one of the most promising approaches of carbon dioxide reduction to mitigate the greenhouse effects [2–4]. Indeed, catalysts play a key role in development of RWGS process. Common catalysts (supported metals systems) [3,5–7] are limited by poor sintering properties, low conversion rate, low selectivity, and the fact that methane is commonly formed as an undesired side product. Comparatively, some metal oxides (e.g. ceria catalysts) exhibit good oxygen storage and oxygen release capabilities. Carbon dioxide can be converted to CO by the capture and disassociation of oxygen on the oxygen vacancies of metal oxides [8]. In this case, these metal oxides show high selectivity to CO, but low reaction activity with CO₂ [9–11].

Cerium oxide has three crystal planes ((100), (110) and (111)). Theoretical work [12] has demonstrated that the formation energies for anion vacancies for cerium oxide surfaces are given as (111) > (110) > (100). Therefore, a desirable goal for the design and synthesis of cerium oxide would be to decrease the number of less reactive crystal planes

and increase the number of more reactive ones so as to optimize the desired structure of the active sites. Ceria nanomaterial with size and shape control has attracted much attention [13–15]. For instance, Soykal et al. [16] and Moraes et al. [17] found that ceria nanocube exhibited good reducibility and oxygen mobility and improved the dispersion of metals, leading to superior performance of steam reforming of ethanol. Recently, although CeO₂-based catalysts (CeO₂ is used as a support or a dopant) have been applied in the conversion of CO₂ elsewhere [18–21], the use of nano-ceria with exposure of specific crystal planes, as catalyst of RWGS, has not yet been reported, and very little is known for the morphology or crystal plane effects of ceria on RWGS reaction.

In the present work, a hydrothermal method was successfully used to synthesize ceria nanomaterial with a well-defined nanocube structure enclosed by (100) planes. We presented the effects of the morphology and crystal plane of ceria on catalytic efficiency of RWGS and discussed the catalytic pathways of RWGS on ceria nanocrystal, especially emphasized the role of oxygen vacancy in ceria.

2. Experimental

2.1. Catalyst Preparation

Three types of ceria materials were prepared by a hydrothermal method. 1.736 g of Ce(NO₃)₃·6H₂O was dissolved in 70 mL of distilled water, and 19.200 g of NaOH was dissolved in 10 mL of distilled water. These two solutions were then mixed and stirred until the formation of milky slurry. The solution was transferred into a 100 mL Teflon beaker and sealed in a stainless steel autoclave. The mixture was heated

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for 24 h at either 373 K or 453 K to obtain nanorods or nanocubes, respectively. To obtain CeO₂ nanooctahedra, the NaOH in this process was substituted for CH₃COONH₄ and heated for 24 h at 453 K. The final products were collected by centrifugation, and washed with deionized water and ethanol to remove any possible ionic remnants. After drying at 333 K for 24 h, the products were calcined at 673 K for 4 h in a nitrogen flow.

Ni/ceria nanocube catalyst was prepared by incipient wetness impregnation of the support with an aqueous solution of Ni(NO₃)₃•6H₂O in order to obtain 1 wt.% of Ni. After impregnation, the sample was calcined at 673 K for 4 h in an air flow.

2.2. Catalyst Characterization

The powder X-ray diffraction patterns (XRD) of ceria were recorded on a Rigaku SmartLab 3KW powder diffractometer using Cu K α radiation at 40 kV and 30 mA. Specific surface area and pore size of the catalyst were studied by nitrogen adsorption/desorption at 77.35 K using an autosorb iQ analyzer. The FT-IR transmission spectrum was recorded with a SHIMADZU FTIR-8400s instrument. SEM analyses of the catalysts were carried out using a field emission scanning electron microscope (FE-SEM) Hitachi SU8000. The morphology structures of particles were observed on a Hitachi H-7650 transmission electron microscope (TEM), operating at 120 kV. X-ray photoelectron spectrometer (XPS) measurements were carried out in an ion-pumped chamber of a Physical Electronics PHI Quantum-2000 spectrometer, employing Al-K α radiation.

2.3. Catalytic activity measurement

The catalytic activities for RWGS were evaluated in a fixed-bed continuous-flow microreactor at atmospheric pressure. Reaction products and the feed stream were analysed by gas chromatography (EChrom A90). The volume of the loaded catalyst was 5.0 ml. Before testing, catalysts were reduced in an 80% H₂/N₂ (60 mL/min) gas flow at 400 °C for 1 h. Sequentially, the mixed gas of CO₂ and H₂ (H₂:CO₂ = 1:1) was fed into the microreactor at a rate of 100 ml/min.

The experimental data were processed by an internal standard method taking nitrogen as the internal standard substance. The conversions of CO₂ (C_{CO₂}) and H₂ (C_{H₂}) and the selectivities of CO (S_{CO}) and CH₄ (S_{CH₄}) were calculated by the following formulae:

$$C_{\text{CO}_2} = \frac{n_{\text{CO}_2}^{\text{in}} - n_{\text{CO}_2}^{\text{out}}}{n_{\text{CO}_2}^{\text{in}}} \quad (1)$$

$$C_{\text{H}_2} = \frac{n_{\text{H}_2}^{\text{in}} - n_{\text{H}_2}^{\text{out}}}{n_{\text{H}_2}^{\text{in}}} \quad (2)$$

$$S_{\text{CO}} = \frac{n_{\text{CO}}^{\text{out}} - n_{\text{CO}}^{\text{in}}}{n_{\text{CO}_2}^{\text{in}} - n_{\text{CO}_2}^{\text{out}}} \quad (3)$$

$$S_{\text{CH}_4} = \frac{n_{\text{CH}_4}^{\text{out}} - n_{\text{CH}_4}^{\text{in}}}{n_{\text{CO}_2}^{\text{in}} - n_{\text{CO}_2}^{\text{out}}} \quad (4)$$

where n_x^{in} or n_x^{out} is the number of mole of x (x = H₂, CO, CO₂ or CH₄) in products or feed gas, respectively.

3. Results and discussion

3.1. Characterization of ceria nanocube

Fig. 1 depicts the FT-IR spectra of as-dried precursor and as-calcined sample. An absorption peak appearing at around 1630 cm⁻¹ and a broad adsorption peak at around m⁻¹ should be assigned to the bending and

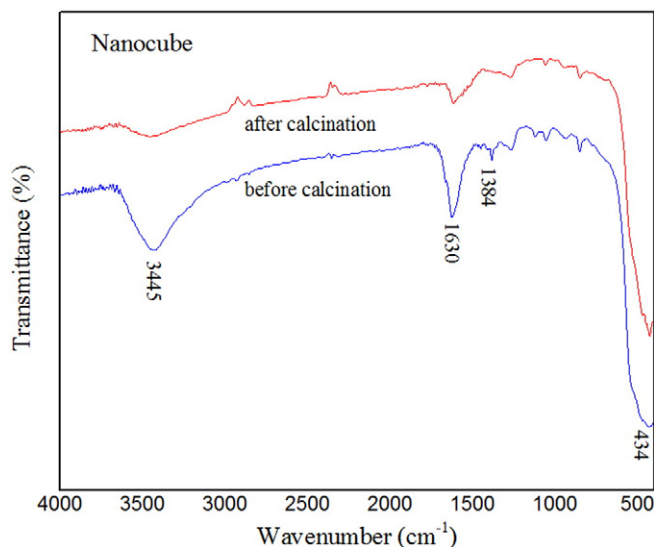


Fig. 1. FT-IR spectra of as-dried precursor and as-calcined ceria nanocube.

stretching modes of the Ce–O bond. Peak at 1384 cm⁻¹ was due to the asymmetrical extensional vibration of residual NO₃⁻. For as-calcined ceria, the impure peaks disappeared or weakened, which indicated that all of the cerium precursors had been converted to ceria after calcination.

Fig. 2 shows the XRD pattern of ceria nanocube. All of the peaks can be well-indexed to (111), (200), (220), (311), (222), (400), (331) and (420) phases, corresponding to a fluorite structure belonging to the cubic lattice system with an Fm-3m space group (JCPDS card No. 34-0394). Measurement of nitrogen adsorption/desorption showed that the obtained ceria nanocube has 42.24 m²/g of specific surface area, 0.324 cm³/g of pore volume, and 31.18 nm of pore size, being a typical mesoporous material.

In Fig. 3, the obtained ceria nanomaterial exhibited clearly cuboidal morphology with a smooth surface and a less-uniform side size of approximately 30 to 150 nm. Mai et al. [22] and Bhatta et al. [23] found that ceria cuboidal nanoparticles synthesized by similar procedure

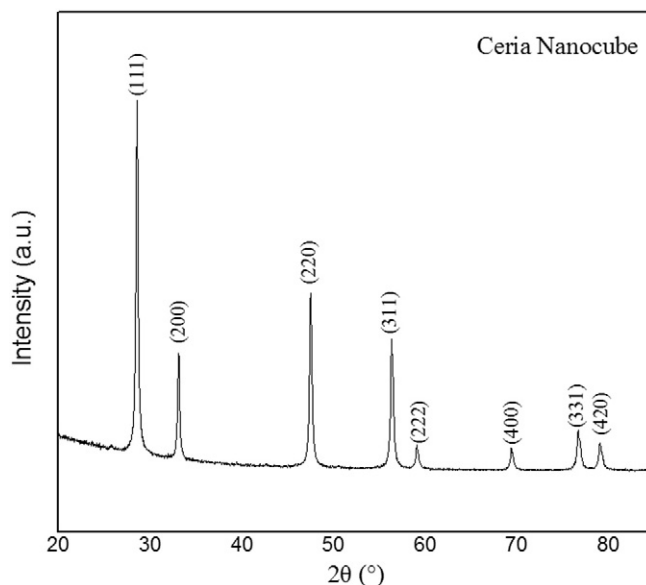


Fig. 2. XRD pattern of as-obtained ceria nanocube.

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