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Mesostructured CeO_2 and Pd/CeO_2 nanophases: Templated synthesis, crystalline structure and catalytic properties

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Abstract

This work reports a ceria solid and Pd/ceria catalyst prepared through a surfactant-templated synthesis route used for simultaneous abasement of NO and CO emissions. The surface features, textural properties and crystalline structure of ceria and Pd/ceria catalyst were studied by means of thermogravimetric analysis (TGA), N_2 physisorption isotherms and in situ Fourier transform infrared (FT-IR) spectroscopy, high resolution electron transmission microscopy (TEM) and X-ray diffraction (XRD) techniques. In the calcination procedure, part of the adsorbed water on the surface of the solid was derived into unidentate and bidentate hydroxyls associated with surface cationic ions of ceria. The surfactant cations were strongly interacted with the solid during the preparation, which induces defects formation in the crystalline structure of the annealed ceria. The retained surfactant in the solid could be combusted to yield CO_2, water and organic molecules with a small amount of coke-like deposits. The resultant ceria showed mesoporous texture and cubic phase containing lattice defects in the crystalline structure. The Pd/CeO_2 catalyst was very active for NO reduction via CO with a high selectivity to N_2. A 100% NO conversion with a selectivity to 100% N_2 was achieved over the Pd/ceria catalyst at a reaction temperature of 300 °C. The catalytic activity and selectivity of this catalyst are much superior to the catalysts of Pt or Rh supported on TiO_2, Al_2O_3, TiO_2–Al_2O_3 and ZrO_2–Al_2O_3 prepared by a sol–gel method. A possible reaction mechanism of NO reduction by CO over the Pd/CeO_2 catalyst was discussed.
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Keywords: Surfactant-templated synthesis; Pd/ceria; Catalyst; NO reduction; CO oxidation

1. Introduction

A novel synthesis approach of mesoporous Si-MCM-41 materials by using organic molecule as synthetic template reported by Mobil scientists, opens new possibilities in the design of innovative materials with potential applications in a variety of areas [1]. By using similar or modified synthesis route, a number of other metal oxides with mesoporous structures were successfully obtained, these include titania [2], zirconia [3], niobia [4], ceria [5], alumina [6], tin oxide [7] and manganese oxide [8]. Since the enhancement of surface area and controllable porosity, these mesostructured metal oxides are very attractive for catalysis. Among these oxides, ceria is particularly interest in a variety of catalytic processes [9]. For instance, ceria has been used as catalyst or support in the selective oxidation, fine chemicals synthesis, methane steam reforming, phenol hydrogenation at atmospheric pressure and solid oxide fuel cell applications [10–14].

One of the important applications of ceria is the use in the area of environmental catalysis, particularly in the design of the new generation of three-way catalysts for simultaneously controlling NO, CO and hydrocarbon emissions in oxygen-rich conditions. This is because ceria has large oxygen storage capacity and the ability of fast transferring bulk oxygen to its surface [15,16], the former may uptake oxygen

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under fuel-lean conditions and the latter may release oxygen under reducing conditions, those allow a ceria-containing catalyst to efficiently work in a relatively wide window of oxygen partial pressure. In addition, ceria may also improve metal dispersion on it and promotes surface and bulk oxygen reducibility of the support when it was used as catalysts additive [17,18]. All of these properties are very important for three-way catalysts for the abatement of automobile exhausts.

Differing from ideas used in the traditional synthesis methods, ceria obtained by using a surfactant-templated synthetic approach shows larger surface area and ordered mesopore structure [5,14]. The mesoporous support of ceria would give rise to stable and well dispersed metal particles on its surface, as a result, enhancement of catalytic performance may be achieved. It is reported that CO conversion on the Pd/ceria prepared by using myristyltrimethylammonium bromide as synthetic template is always higher than that achieved on the one prepared by using a precipitation method, this resulted from larger surface area and better metal dispersion [5].

In the current work, mesoporous ceria nanophase was obtained in a base condition, through a templated synthesis route, using cetyltrimethylammonium chloride as the template. The surface features and texture properties of the resultant ceria are characterized by thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), Brunaur–Emmett–Teller (BET) and transmission electron microscope (TEM) techniques. Its crystalline structure was refined by applying Rietveld method on the basis of X-ray diffraction (XRD) analysis. Evidence of surfactant association with the pores of the solid is provided and the catalytic activity and selectivity of NO reduction via CO over the ceria and Pd/ceria catalyst are reported.

2. Experimental

2.1. Ceria preparation

To prepare ceria solid, two solutions were prepared: the first solution was prepared by dissolving 16.0 g of cetyltrimethylammonium chloride (CH_3–$(CH_2)_{15}N(CH_3)_3Cl$, referred as CTACl) in 500 ml deionized hot water (around 50 °C) with stirring, followed by adding 120 ml of aqueous ammonia (28 wt.%) to obtain a clear micellar solution; the second solution was prepared by dissolving 21.7 g of $Ce(NO_3)_3{\cdot}6H_2O$ in 500 ml deionized water. The cerium solution was added, drop-by-drop, into the surfactant solution with a proper agitation to disperse the droplets before local concentrations become excessive. The pH value of the mixture remained at approximately 11 in order to induce the hydrolysis and the polycondensation of the inorganic precursor around the formed micelles. Afterwards, the slurry was continuously stirred for 4 h until gel was formed, and then it was sealed in a Teflon bottle for hydrothermal treatment at 100 °C for 5 days. The solid was then filtered and washed with water and methanol for several times. The resultant material was dried at 80 °C for 24 h and then was calcined at 200, 400 and 600 °C for 4 h for further characterization.

2.2. Preparation of 3 wt.% Pd/CeO_2

The 3 wt.% Pd/CeO_2 catalyst was prepared by impregnating the ceria support annealed at 600 °C with a calculated amount of an aqueous solution of $Pd(NO_3)_2{\cdot}2H_2O$. The metal supported catalyst was dried at 120 °C for 4 h and then was calcined at 600 °C for 4 h. Before the catalytic test, the catalyst was reduced by using 99.9% H_2 at 400 °C for 1 h in order to obtain metallic palladium particles on the catalyst.

2.3. Textural properties

The textural properties of the ceria solids were measured in a Digisorb 2405 sorptometer by means of N_2 physisorption isotherms at −195 °C. Before the N_2 adsorption, 0.5 g of the sample was thermally treated at 200 °C under vacuum condition for 6 h in order to remove water from the sample. The surface area was determined according to the standard Brunaur–Emmett–Teller method and the total pore volume was evaluated from the amount of adsorbed N_2 at a relative pressure (P/P_0) of about 0.99. The pore diameter distributions were calculated based on the desorption isotherms by the Barrett–Joyner–Halenda (BJH) algorithm.

2.4. Analysis of thermogravimetric–Fourier transform infrared (TG–FT-IR)

TG analysis was carried out in flow air using a Dupont Model 950 thermoanalyzer from 25 to 800 °C at a heating rate of 20 °C/min to determine weight losses during the thermal treatment and to verify if the CTACl incorporation with the solid materials. The gaseous products produced during TG procedure were simultaneously monitored by means of an on line coupled FT-IR spectroscopic technique.

2.5. Surface characterization by in situ FT-IR

The surface dehydroxylation and removal of the residual surfactants from the dried samples were characterized by using in situ FT-IR spectroscopic technique on a Nicolet Magna-IR 550 spectrometer. The sample was ground by hand with a pestle in a mortar and then pressed at 4 tonnes to give a self-supporting wafer (10 nm in diameter). The sample wafer (around 10 mg) was placed inside an IR cell, which was coupled with a vacuum and heating systems. The sample could be exposed to various gaseous environments with different pressures at different temperatures not exceeding 400 °C. The in situ FT-IR spectra reported herein were recorded at 25, 100, 200, 300 and 400 °C, respectively.

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