Microporous and Mesoporous Materials 119 (2009) 158–164

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Synthesis of mesoporous $Ce_{1-x}Zr_xO_2$ ($x = 0.2-0.5$) and catalytic properties of CuO based catalysts

Meiling Teng [a], Laitao Luo [a,*], Xiaomao Yang [b]

[a] Department of Chemistry, Nanchang University, Nanchang 330031, PR China
[b] Institute of Applied Materials, College of Resource and Environment Management, Jiangxi University of Finance and Economics, Nanchang 330013, PR China

ARTICLE INFO

Article history:
Received 18 July 2008
Received in revised form 1 October 2008
Accepted 20 October 2008
Available online 31 October 2008

Keywords:
Polyol method
Mesoporous $Ce_{1-x}Zr_xO_2$
CuO
CO selective oxidation
H_2-rich gas

ABSTRACT

Mesoporous $Ce_{1-x}Zr_xO_2$ (m-$Ce_{1-x}Zr_xO_2$, $x = 0.2-0.5$) mixed oxides were synthesized by using polyol method. The influences of coefficient x on performances of m-$Ce_{1-x}Zr_xO_2$ and Cu based catalysts towards CO selective oxidation in H_2-rich gas were investigated. The samples were characterized by means of XRD, Raman, FT-IR, TG, BET, TEM, TPR and TPD techniques. The results showed that all m-$Ce_{1-x}Zr_xO_2$ samples were mesoporous materials with cubic fluorite-structure, and the highest surface area (181 $m^2\,g^{-1}$) was obtained when the $x = 0.5$. Compared with CuO/m-$Ce_{1-x}Zr_xO_2$ ($x = 0.2-0.35$) catalysts, the CuO/m-$Ce_{0.5}Zr_{0.5}O_2$ catalyst had higher CO conversion and selectivity in H_2-rich gas, they were 100% and 96.2% at 383 K, respectively. This is explained in terms of its stronger interaction between active ingredient and support, higher dispersion, more active sites, larger CO adsorption amount and lower desorption temperature, which were advantageous to enhance its catalytic activity.

1. Introduction

Materials containing ceria are attracting our much attention because of their either as catalysts and/or oxygen storage/release components in the formulation of catalysts for the control of emissions from automobiles [1], solid oxide fuel cells [2], ceramic [3], and so forth. Binary metal oxides of ceria and zirconia are particularly interesting due to their unique redox properties, high oxygen storing/releasing capacity and high thermal stability. There are many different synthetic methods that have been applied to prepare CeO_2—ZrO_2 and related mixed oxides, including solid state synthesis [4], co-precipitation [5], and sol–gel [6]. One of the keys to this success is the selection of an appropriate precursor [7], the preparation methods and the composition (i.e. Ce:Zr ratio), which in turn determine homogeneity at a molecular level, surface area and textural/morphological properties. After the discovery of the silica-based mesophases, MCM-41 [8] and FSM–16 [9], highly-ordered mesoporous ceria and mesoporous ceria–zirconia materials were synthesized by surfactant-assisted and templating methods [10]. In addition, highly-ordered mesoporous ceria–zirconia thin films were reported in 2003 [11], and hierarchically mesoporous/macroporous materials of alumina, Titania, silica, zirconia, aluminosilicate were also synthesized [12]. Recently, the fabrication of thermally stable hierarchically-ordered porous materials has attracted researcher's considerable attention because of their good catalytic performances. Herein, we report the synthesis of a highly thermally stable, hierarchically-ordered, meso-structured, CuO-loaded ceria–zirconia catalyst by using a new polyol method. The background of this method is the precipitation of a solid while heating sufficient precursors in a multivalent and high-boiling alcohol .The alcohol itself acts as a stabilizer, limiting particle growth and prohibiting agglomeration. Ethylene glycol has been widely used in the polyol synthesis of metal nanoparticles because of its physical properties: (1) a high dielectric constant, which enhances the solubility of inorganic salts; (2) a high-boiling point (468 K at atmospheric pressure), which makes it possible to carry out at the preparation of inorganic compounds at relatively high temperatures; and (3) its strong reducing power. More over the synthesis is comparably easy to perform.

Developing efficient catalysts for the selective oxidation of carbon monoxide in the presence of excess hydrogen is a challenge in research on the heterogeneous catalysis of the preparation of H_2 used in polymer electrolyte membrane fuel cells (PEMFC) [13,14]. Hydrogen is used as a fuel in the PEMFC system, and ideally, the reaction product is only H_2O. Hydrogen is generally generated from steam/autothermal reforming or partial oxidation of hydrocarbons or methanol, followed by a water–gas shift reaction [15]. Typical effluents from such a process contain 0.3–1% of CO in excessive H_2 (40–75%). Carbon monoxide must be removed to avoid poisoning the anode electro-catalysts [16,17]. The selective oxidation of CO with O_2 appears to be the simplest and most effective method for removing CO. Mixed oxides of CuO—CeO_2 have recently been proposed as good candidates for the selective removal of CO from

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[*] Corresponding author. Tel.: +86 06 791 3969514.
E-mail address: luolaitao@163.com (L. Luo).

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doi:10.1016/j.micromeso.2008.10.019

reformate streams [18,19]: they can be used in the temperature range of 373–423 K with a selectivity of 90–95% for complete conversion; they are more active and significantly more selective than Pt-based catalysts at a lower reaction temperature, they are less active but much more selective than Au-based catalysts. The use of the mixed oxide CuO—CeO_2 in CO oxidation has recently attracted researcher's much attention. Zr^{4+} in the lattice of CeO_2 forms a solid solution. Hori et al. [20] found that the beneficial effects of ZrO_2 occurred in solid solutions of $Ce_{1-x}Zr_xO_2$ that had oxygen capacities three to five times higher than those of the pure CeO_2. Zr^{4+} increased the capacity of redox property, so CuO supported on $Ce_{1-x}Zr_xO_2$ was expected to enhance CO oxidation.

Yan et al. reported that mesoporous $Ce_{0.2}Zr_{0.8}O_2$ nanoparticles synthesized by the hydrothermal method showed a blue-shift in UV absorption and high CO conversion activity [21]. Furthermore, better crystal phase homogeneity leads to higher oxygen capacity and thermal stability. Thus, we used mesoporous $Ce_{1-x}Zr_xO_2$ as supports and CuO/m-$Ce_{1-x}Zr_xO_2$ as catalysts towards CO selective oxidation in H_2-rich gas. In this study, polyol method was applied to prepare high surface area meso-structured ceria–zirconia catalysts. The influence of structural parameters on thermal catalytic performance was also discussed.

2. Experimental

2.1. Preparation of mesoporous $Ce_{1-x}Zr_xO_2$ (x = 0.2–0.5)

Mesoporous $Ce_{1-x}Zr_xO_2$ ($x = 0.2-0.5$, m-$Ce_{1-x}Zr_xO_2$) were prepared by glycol method. A certain amount of ammonium cerium (IV) nitrate and zirconium oxychloride were dissolved in 60 mL of ethylene glycol containing 0.16 M poly(vinylpyrrolidone) (PVP *M*w 10,000) under vigorous stirring until a homogeneous colorless solution was obtained. The mixture was refluxed for 7 h at 463 K, filtered and washed with deionized water and ethanol to remove excess ethylene glycol and PVP. The obtained sample was dried at 373 K overnight and calcined at 673 K in air atmosphere for 4 h.

Non-mesoporous $Ce_{0.5}Zr_{0.5}O_2$ was prepared by a co-precipitation method. A certain amount of ammonium cerium (IV) nitrate and zirconium oxychloride were dissolved in deionized water. Under stirring, 27 wt.% ammonia solution was added dropwise until pH of the mixture remained at approximately 11. The precipitate was filtered and washed with deionized water thoroughly. Then, it was dried at 373 K overnight, and subsequently calcined at 673 K in air atmosphere for 4 h. The prepared sample was designated as cp-$Ce_{0.5}$ $Zr_{0.5}O_2$.

2.2. Preparation of CuO based catalysts

The CuO based catalysts were prepared by incipient wetness impregnation method. m-$Ce_{1-x}Zr_xO_2$ (or cp-$Ce_{0.5}Zr_{0.5}O_2$) support was impregnated with a copper nitrate solution, followed by 12 h drying (373 K) and 4 h calcination (673 K). The loading of CuO in CuO/m-$Ce_{1-x}Zr_xO_2$ and CuO/cp-$Ce_{0.5}$ $Zr_{0.5}O_2$ catalysts is 5.0 wt.%.

2.3. Characterization

Powder X-ray diffractometer (German Bruker-AXS Corporation D8) (operating at 40 kV and 30 mA) was used at room temperature using Cu Kα radiation combined with the nickle filter. The crystal size was calculated by Scherrer formula ($d = k\lambda/B_{1/2}\cos\theta$).

BET surface area and porous texture were evaluated by N_2 adsorption isotherms obtained at 77 K using an ASAP2020 (micromeritics) equipment. Before each measurement, the samples were degassed at 623 K in vacuum (0.13 Pa) for 1.6 h.

The IR spectra and the Raman spectra were recorded by a Nicolet 5700 Fourier transform instrument and NXR–FT Raman spectrometer.

TEM images were achieved on a JEM-2010 at 120 kv. A trace amount of sample was suspended in ethanol solution, followed by sonication for 10 min. Carbon-coated copper grids were used as the sample holders.

Temperature-programmed reduction (TPR) was carried out in Micromeritics of Chemisorb 2750 over 0.02 g catalyst. The samples were heated from room temperature to 1073 K in N_2 (40 mL/min) at a rate of 10 K/min in order to remove possible impurities. After cooling to room temperature in N_2, a gas mixture consisting of H_2 and N_2 (10:90 *v*/*v*) was introduced into the system and heated at a rate of 10 K/min for recording the TPR spectra.

Temperature-programmed desorption (TPD) was carried out in-house apparatus over 0.1 g catalysts. The samples were first heated from room temperature to 673 K in Ar (40 ml/min) at a rate of 10 K/min in order to remove possible impurities contained in the samples. After being cooled to room temperature in Ar, CO was injected into the reactor until being saturated with CO. Then the samples were heated to 673 K at a rate of 10 K/min for recording CO–TPD spectra.

Thermogravimetric analysis (TG) measurement was performed on Rigaku TAS-100 Analyzer with a heating rate of 10 K/min under a flow of air.

2.4. Catalytic activity measurements

The CO oxidation reaction in H_2-rich gas was carried out with a flow reactor. For each experiment, 0.1 g catalyst was used. The space velocity was 18,000 ml/h g and the composition of the mixture gases was CO, 2.0 vol.%, O_2, 3.3 vol.%, H_2, 50 vol.%, and N_2, 44.7 vol.%. The gas composition was analyzed before and after the reaction by an on-line gas chromatography with thermal conductor detector (TCD), connected with a computer integrator system and using TDX-01 column. The catalytic activity is assigned as conversion of CO.

3. Results and discussion

3.1. XRD and Raman spectroscopy analysis of $Ce_{1-x}Zr_xO_2$mixed oxides

To determine the structure of m-$Ce_{1-x}Zr_xO_2$ and cp-$Ce_{0.5}Zr_{0.5}O_2$ mixed oxides in detail, the samples were investigated by means of XRD. The low-angle XRD patterns of m-$Ce_{1-x}Zr_xO_2$ ($x = 0.2-0.5$) and cp-$Ce_{0.5}Zr_{0.5}O_2$ mixed oxides are shown in Fig. 1. The diffraction peaks are observed only one at $2\theta = 1.0°$, indicating that the prepared m-$Ce_{1-x}Zr_xO_2$ mixed oxides are typical mesoporous materials, but the absence of a long-range order with regular pore distribution. cp-$Ce_{0.5}Zr_{0.5}O_2$ does not exhibit reflection, suggesting that it is non-mesoporous material.

As is well-known, the $Ce_{1-x}Zr_xO_2$ solid solutions exist in three stable phases (monoclinic (m), tetragonal (t), cubic (c)) and two metastable phases (t', t'') under different conditions [22]. XRD patterns for $Ce_{1-x}Zr_xO_2$ mixed oxides in the different compositional range are compared in Fig. 2. The X-ray diffraction patterns of $Ce_{1-x}Zr_xO_2$ mixed oxides exhibit four peaks around $2\theta = 29$, 33, 48 and 57°, corresponding to the CeO_2 (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes, which indicate the presence of a true mixed oxide phase with the cubic fluorite-structure. There is no evidence of the presence of other phases, which can be due to cation radius of Zr^{4+} (0.084 nm) is smaller than that of Ce^{4+} (0.097 nm), then Zr^{4+} incorporate into CeO_2 lattice. These results are not in agreement with those obtained from Ce—Zr—O prepared by other routes [23]. The average crystallite size calculated by Scherrer equation