Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Molecular Catalysis A: Chemical 243 (2006) 204–213
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Promoting effect of ceria on the physicochemical and catalytic properties of CeO_2–ZnO composite oxide catalysts

Braja Gopal Mishra, G. Ranga Rao *

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

Received 2 May 2005; received in revised form 30 July 2005; accepted 30 July 2005
Available online 23 September 2005

Abstract

CeO_2–ZnO composite catalysts prepared by amorphous citrate method have been investigated for cyclohexanol dehydrogenation and hydrogen transfer reactions. The precursors and catalysts have been characterized by TGA, CHN analysis, XRD, UV–vis–NIR diffuse reflectance, SEM and acid–base measurements. The amorphous precursors in citrate process contain one molecule of citric acid per Ce^{4+} or Zn^{2+} ions. Structural studies of composite oxides indicate the presence of individual oxide phases along with non-equilibrium solid solutions in a limited composition range. The composite oxides contain low coordination Ce^{3+} and Ce^{4+} sites. Cyclohexanone was obtained as main product for cyclohexanol transformation reaction carried out over these mixed oxide catalysts due to dehydrogenation on basic sites. The presence of ceria in the composite oxide enhances the surface area and acid–base properties facilitating the dehydrogenation process. At low ceria content, the CeO_2–ZnO composite oxide catalysts show higher catalytic activity for both cyclohexanol dehydrogenation and hydrogen transfer reactions due to higher basicity, surface area and smaller crystallite sizes. Hydrogen transfer activity is found to be higher on CeO_2(10%)–ZnO catalyst prepared by citrate method compared to the catalyst prepared by decomposition from acetate precursor. This study demonstrates the promoting effect of ceria in CeO_2–ZnO catalysts for reactions involving acid–base sites.

Keywords: CeO_2; ZnO; CeO_2–ZnO; UV–vis–DRS; Cyclohexanol transformation; Hydrogen transfer reaction

1. Introduction

Ceria and ceria-based composite oxide systems have been extensively investigated for catalytic applications such as three-way catalysis, catalytic wet oxidation, water–gas-shift reaction, oxidation/combustion catalysis and solid oxide fuel cells [1–7]. The redox property of ceria plays a prominent role in all these catalyzed reactions. The number of effective redox sites and their ability to exchange oxygen can be manipulated by incorporating transition metal ions into the ceria lattice and promoted by noble metals dispersed on ceria [1,7–10]. Zirconia-incorporated ceria is a good example which shows enhanced reducibility in the presence of noble metals such as Rh, Pt and Pd [11–14]. While the role of ceria has been well established as a redox promoter, there is much scope to investigate the acid–base properties of ceria-based materials. Ceria-based composite oxides have been increasingly studied for their role as acid–base catalyst/promoter for various reactions. The promoting/catalyzing effect of ceria in pure or in the form of composite oxide is attributed to the combination of acid–base and redox properties of ceria. Addition of ceria into MgO has been found to increase the number of effective weak base sites responsible for alkylation reaction [15,16]. Similarly, in the case of CeO_2–CaO composite system, the surface acid–base property is found to increase at low ceria content and the effect is more prominent on acidic sites [17]. The acid–base property of ceria and ceria-based composite oxide materials have been studied by microcalorimetry [18,19], in situ IR study of adsorbed pyridine and CO_2 [20] and model reactions [21]. These studies generally agree that the surface acidic property is due to surface Ce^{4+} and $OH^{\delta+}$ species while the basic property is related to surface O^{2-} and $OH^{\delta-}$ ions [20]. The relative amounts of surface unsaturated cations and the hydroxyl groups contributing to acid–base sites depend on the method of preparation. Sato et al. [15] showed that ceria samples prepared from different precursor salts show different surface areas, acid–base

---

* Corresponding author. Tel.: +91 44 2257 4226; fax: +91 44 2257 4202.
E-mail address: grrao@iitm.ac.in (G.R. Rao).

1381-1169/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2005.07.048

properties and catalytic activity for alkylation of phenol. Martin and Duprez [21] have shown the presence of strong basic sites on ceria and correlated them with oxygen mobility [22]. Microcalorimetric measurements on ceria surface indicate the presence of strong basic sites which are not homogenously distributed. Doping small amount of zirconium in the ceria lattice remarkably modifies the basic character of the solid solution. The $Ce_{0.8}Zr_{0.2}O_2$ phase is reported to exhibit high heat of CO_2 adsorption and homogeneous basic sites [19]. It is therefore clear that the surface properties and catalytic activity of ceria can be improved by synthesizing appropriate ceria-based composite oxides.

The $Ce_{1-x}Zn_xO_{2-x}$ ($x = 0$–0.56) solid solutions prepared by soft chemical route at 40 °C and pH 6 using H_2O_2 as oxidant have shown excellent UV-shielding properties and decreased catalytic oxidation activity [23–25]. In these studies, the incorporation of Zn into CeO_2 lattice is influenced by H_2O_2. We have reported earlier that the presence of small amount of CeO_2 (10 wt.%) in ZnO lattice enhances hydrogen transfer activity of CeO_2–ZnO materials for cyclohexanone using 2-propanol as hydrogen donor [26]. These studies show that the formation of $Ce_{1-x}Zn_xO_{2-x}$ solid solutions and their catalytic activity are strongly influenced by method preparation [23–26]. In continuation of our work, we report here the detailed characterization of CeO_2–ZnO samples in the whole composition range and discuss their catalytic activity for both cyclohexanol transformation and hydrogen transfer reactions. The pure components and mixed oxides with different compositions were prepared by amorphous citrate process. The composite oxides are found to have better physicochemical properties and catalytic activities compared to individual oxide components. A good correlation has been observed between surface properties and catalytic activity of the composite oxide catalysts for cyclohexanol dehydrogenation and hydrogen transfer reactions. The catalytic studies clearly demonstrate the ability of ceria in promoting organic reactions on acid–base sites.

2. Experimental

2.1. Catalyst preparation

$Ce(NO_3)_3\cdot 6H_2O$ (CDH Chemicals, India, 99.9%), $Zn(NO_3)_2\cdot 6H_2O$ and citric acid monohydrate (S.D. Fine Chemicals, India, 99.9%) were used to prepare CeO_2(x mol%)–ZnO mixed oxides. A solid mixture of cerium and zinc nitrates of desired molar ratio was mixed with an equimolar amount of citric acid and heated at 60 °C to form uniform melt which was evacuated to obtain an expanded spongy solid material. This material is transferred to hot air oven at 160 °C for 2 h to obtain amorphous citrate precursor. The calcination of citrate precursor at 550 °C for 3 h produced fine powder of CeO_2–ZnO mixed oxide. Pure ZnO and CeO_2(10%)–ZnO were also prepared from the decomposition of corresponding acetate salts. For preparing CeO_2(10%)–ZnO composite, zinc acetate and cerium acetate salts were dissolved in minimum amount of water to form a thick paste which was dried and calcined at 500 °C in air for 3 h. The ZnO and CeO_2(10%)–ZnO catalysts prepared by this method are designated in the text as ZnO-dec and CeO_2(10%)–ZnO-dec.

2.2. Catalyst characterization

All samples were analysed by X-ray diffraction employing Shimadzu XD-D1 diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). The UV–vis spectroscopic studies were carried out in diffuse reflectance mode. UV–vis–NIR spectra were recorded on a Varian Cary 5E spectrometer equipped with an integrating sphere coated with polytetrafluoroethylene (PTFE) in the spectral range of 200–2500 nm. The powder samples were made into self-supported pellets of 13 mm diameter and 2 mm thick for measurements. Thermogravimetry analysis of the samples were preformed on Perkin-Elmer TGA-7 apparatus in air (30 ml/min) with linear heating rate (20 °C/min) from room temperature to 800 °C. The CHN analysis of the amorphous citrate precursor was carried out on a Heraeus-CHN-rapid analyzer. Scanning electron microscopy pictures were taken using JEOL JSM-5300 microscope (acceleration voltage 15 kV). The sample powders were deposited on a carbon tape before mounting on a sample holder. The surface acidity and basicity of the composite oxide catalysts were determined by employing titration method [27]. Prior to the acid–base measurement, the catalyst samples were calcined at 500 °C in high pure nitrogen and cooled to room temperature. The standard solutions of *n*-butylamine and trichloroacetic acid were prepared in double distilled dry benzene. 0.5 g of oxide catalyst was kept for equilibration separately with 0.025 M of *n*-butylamine and trichloroacetic acid solutions for 24 h. The acid–base property of the catalysts was evaluated by mutual titration employing neutral red as indicator. The acidity and basicity of catalyst samples were obtained in mmol g^{-1} from the respective equivalent volumes of *n*-butylamine and trichloroacetic acid consumed.

2.3. Catalytic activity studies

The vapour phase cyclohexanol dehydrogenation and hydrogen transfer reactions of cyclohexanone with 2-propanol were carried out using 0.4–1.0 g catalyst packed in a fixed bed flow glass reactor. The reaction temperature was continuously monitored by a thermocouple placed in the middle of the catalyst bed. Prior to the reaction, the catalysts were activated in oxygen flow (25 ml/min) for 3 h at 450 °C and brought to the reaction temperature. The reactants were fed through the top of the reactor by means of a motor driven infusion pump (SP2S-MC model, Electronic Corporation, India). Pure nitrogen was used as a carrier gas at a flow rate of 30 ml/min. The liquid products were collected in an ice trap and analyzed by gas chromatograph (AIMIL-Nucon 5765, India) using flame ionization detector and 20% carbowax column. The column temperature was controlled from 70 to 190 °C at a linear heating rate of 10 °C/min. Each reaction run continued for 1 h and at the end of the each run catalysts were reactivated at 450 °C in oxygen for 3 h for a subsequent run.