



Nanosized $Ce_{1-x}La_xO_{2-\delta}/Al_2O_3$ solid solutions for CO oxidation: Combined study of structural characteristics and catalytic evaluation

Lakshmi Katta, T. Vinod Kumar, D. Naga Durgasri, Benjaram M. Reddy*

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Uppal Road, Hyderabad 500 607, India

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ABSTRACT

Nanosized lanthanum-doped ceria ($Ce_{1-x}La_xO_{2-\delta}$) and the same dispersed on alumina support ($Ce_{1-x}La_xO_{2-\delta}/Al_2O_3$) were synthesized following a simple and high yielding procedure. Formation of solid solutions and interaction with the support were monitored by X-ray diffraction (XRD), Raman spectroscopy (RS; UV-RS and Vis-RS), high-resolution electron microscopy (HREM), Brunauer–Emmett–Teller (BET) surface area, X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR) and diffuse reflectance spectroscopy (UV-DRS) techniques. XRD results confirmed the formation of ceria–lanthana solid solutions. HREM studies revealed well distributed and small sized Ce–La–oxide particles of ~ 7 nm size over the surface of alumina support. Formation of defect sites or oxygen vacancies was investigated by RS using 325 and 632.81 nm excitation laser lines which confirmed their presence in the investigated samples. RS studies further deduced that evolution of oxygen vacancies ($\sim 570\text{ cm}^{-1}$) was due to different ionic valence state of dopant (La^{3+}) from that of Ce^{4+} , while the development of MO_8 -type complex ($\sim 600\text{ cm}^{-1}$) was due to different ionic radius of dopant (La^{3+} , 0.110 nm) from that of Ce^{4+} (0.097 nm). XPS results suggested that there is no significant change in the Ce^{3+} amount during thermal treatments due to the absence of undesirable cerium aluminates formation. TPR data revealed that surface modification with support enhances the reducibility of the doped ceria. Catalytic evaluation showed a 50% CO conversion temperature of 634 K per 66 mg of CL for the CL/A catalyst, which is lower than the CL sample (636 K per 100 mg of CL), possibly on account of an increased dispersion, more oxygen vacancies and easy reducibility.

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1. Introduction

The environmental legislation has imposed stringent targets for permitted levels of atmospheric emissions. The removal of detrimental gases (CO, NO_x , HC, etc.) from the automobile exhausts is therefore an immense commendable task. Among these, the complete oxidation of carbon monoxide is of prime importance to meet increasingly stringent environmental regulations in a practical way. The catalysts being mostly studied for these processes are supported Pd, Pt and Rh based catalysts; however, the rarity and cost of these catalysts are posing serious problems to the implementation of clean energy technologies on a large scale. Therefore, there is an ongoing search for inexpensive and highly active catalysts for CO oxidation and other related applications [1].

Ceria (CeO_2) has long been regarded as one of the key materials in modern catalysis due to its ability to cycle easily between reduced and oxidized states (i.e. $Ce^{3+} \leftrightarrow Ce^{4+}$) in combination with numerous oxygen vacancies [2–5]. This eminent feature has been

considered as the heart of the material which makes present automotive exhaust treatment catalysts containing ceria much more effective than their predecessors. Further, nanosized ceria has been reported to be active for free-radical scavenging and oxidase-like activity in bio-systems [6,7]. Recently, it has also been employed as a redox catalyst for thermochemical production of chemicals using solar energy [8]. However, pure ceria is poorly thermostable and undergoes rapid sintering under high-temperature conditions thereby loses its crucial oxygen storage/release capacity (OSC). The most important strategy to tackle this problem is to modify ceria with other elements. The key parameters that are important when doping the ceria with any other oxide are (i) the dopant ion concentration and (ii) size and/valence of the dopant ion to achieve optimum reducibility [5]. With respect to undoped oxide, doped ceria with cations of different size or charge alter ion mobility inside the modified lattice, resulting in the formation of non-stoichiometric defective fluorite-structured solid solutions. Such amendments in the defect structure of ceria confer new properties to the catalyst such as better resistance to sintering at high temperatures and a decrease in the activation energy for oxygen vacancy formation during reduction. Thus, incorporation of appropriate dopants into the ceria lattice results in the formation of new

* Corresponding author. Tel.: +91 40 2719 1714; fax: +91 40 2716 0921.

E-mail addresses: bmreddy@iict.res.in, mreddyb@yahoo.com (B.M. Reddy).

stable compounds leading to different physicochemical properties and catalytic behavior [9,10].

Among various dopants, lanthana has attracted considerable attention recently. Mackrodt et al. first observed a noticeable improvement in the catalytic activity of ceria–lanthana solid solutions for combustion of methane [11]. Lanthanum and cerium are the nearest homologous elements and both belong to lanthanide series, which exhibit fine chemical tuning property [12]. However, a large difference in the ionic radii between La^{3+} and Ce^{4+} is expected to induce huge lattice deformation and promote the oxygen vacancy (charge compensation mechanism) generation in the ceria lattice which can facilitate more channels for oxygen flow, together serve as key factors for oxidation reactions. To further increase the surface area and to sustain high activity under real conditions, ceria-based systems are usually supported on transition aluminas ($\sim 127 \text{ m}^2/\text{g}$), with the aim of achieving good dispersion of the active phase and enhancement in the oxygen exchange rate.

The present investigation was undertaken against the aforesaid background. Accordingly, the primary goal of the present study was to understand the influence of support on the catalytic activity of La^{3+} doped ceria. For this purpose, nanosized $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ (CL) and $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}/\text{Al}_2\text{O}_3$ (CL/A) solid solutions were synthesized by coprecipitation and deposition coprecipitation methods, respectively and evaluated for CO oxidation. The physicochemical properties were investigated by using a variety of techniques including Brunauer–Emmett–Teller (BET) surface area, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), UV–visible diffuse reflectance spectroscopy (UV–vis DRS), Raman spectroscopy and temperature programmed reduction (H_2 -TPR).

2. Experimental

2.1. Catalyst preparation

The investigated ceria–lanthana (CL; 8:2 mole ratio based on oxides) and ceria–lanthana/alumina (CL/A; 8:2:10 mole ratio based on oxides) samples were prepared by coprecipitation and deposition coprecipitation methods, respectively using cerium(III) nitrate (Aldrich, AR grade) and lanthanum(III) nitrate (Aldrich, AR grade) precursors. At first, the desired quantity of powdered γ -alumina (Harshaw, specific surface area $\sim 127 \text{ m}^2/\text{g}$) was dispersed in about 2000 ml of deionized water and stirred for 2 h. Requisite amounts of cerium and lanthanum precursors were dissolved separately in 500 ml of deionized water, mixed together and stirred continuously for 1 h. Under stirring conditions, the nitrate precursor solutions and the dispersed alumina solution were thoroughly mixed and the whole mixture was diluted to 4000 ml with deionized water. Upon completion of mixing, an excess amount of ultra diluted ammonium hydroxide was added dropwise resulting in a pH of ~ 8.5 . The obtained precipitates were filtered off and washed several times with deionized water until free from anion impurities. The obtained cake was oven-dried at 393 K for 12 h and calcined at 773 K for 5 h. The calcined mixed oxides were once again heated at 873, 973 and 1073 K for 5 h. For comparison, ceria sample was also prepared following the same procedure under identical conditions.

2.2. Catalyst characterization

XRD data was acquired in the 2θ range of $12\text{--}80^\circ$ on a Rigaku Multiflex instrument using $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation and a scintillation counter detector. The average crystallite size of CL and CL/A samples were estimated with the help of Debye–Scherrer equation using the XRD data of all prominent lines, and the cell

parameter 'a' was calculated by a standard cubic indexation method using the intensity of the base peak (1 1 1) [13,14]. High-resolution electron microscopy (HREM) studies were made on a JEM-2010 (JEOL) instrument equipped with a slow-scan CCD camera and at an accelerating voltage of 200 kV. The Raman spectra were obtained at room temperature using a LabRam HR800UV Raman spectrometer (Horiba Jobin-Yvon) fitted with a confocal microscope and liquid-nitrogen cooled charge-coupled device (CCD) detector. The BET surface areas were determined by adsorption isotherms at liquid N_2 temperature (77 K) recorded on SMART SORB-92/93 instrument via a thermal conductivity detector. The XPS measurements were performed on a Shimadzu (ESCA 3400) spectrometer by using $\text{Mg K}\alpha$ (1253.6 eV) radiation as the excitation source. Charging of catalyst samples was corrected by setting the binding energy of the adventitious carbon (C 1s) at 284.6 eV. The XPS analysis was done at ambient temperature and pressures usually in the order of less than 10^{-8} Pa. The UV–vis DRS measurements were conducted over the wavelength range of $\lambda = 200\text{--}750 \text{ nm}$ using a GBS-Cintra 10e UV–vis NIR spectrophotometer with an integration sphere diffuse reflectance attachment. Sample was diluted in a KBr matrix by pelletization. Reducibility of the samples was examined by H_2 -TPR using thermal conductivity detector of a gas chromatograph (Shimadzu) in a conventional lab apparatus. About 30 mg of sample mass was loaded in an isothermal zone of the reactor and heated at a rate of 10 K/min to 473 K using 30 ml/min helium gas flow which facilitated to drive away the molecules that had been pre-adsorbed on the surface of the catalysts. After the sample was cooled to room temperature, the helium was switched to 5% H_2/Ar with a rate of 20 ml/min and the temperature was linearly raised to 1073 K at a continuous heating ramp of 5 K/min. The hydrogen consumption during the reduction process was calculated by passing the effluent gas through a molecular sieve trap to remove the produced water and then to TCD.

2.3. Catalyst evaluation

The catalytic performance of the sample for CO oxidation was conducted at normal pressure in the temperature range 300–773 K @ 5 K/min using a fixed bed reactor of micro activity. About 100 mg catalyst sample (250–355 μm sieve fraction) was diluted with quartz particles of the same sieve fraction and placed in a quartz reactor. The total flow rates (9.98% CO and 10.2% O_2 balanced with argon) maintained by three mass flow controllers were in the range of 50–60 sccm (standard cubic centimeters per minute). The CO and CO_2 gas concentrations were measured using an Uras 14 infrared analyzer module, and the O_2 concentration was measured using a Magnos 16 analyzer (Hartmann & Braun). Prior to oxidation of CO, the catalyst was heated to 773 K in 10.2% O_2/Ar gas mixture, using a heating ramp of 10 K/min, and kept at the final temperature for 1 h. Then the oxidized sample was purged in argon. Partial pressures of CO and O_2 were in the range of 10 mbar.

3. Results and discussion

XRD analysis provides information corresponding to crystallographic structure, structural deformation, solid solution formation and crystallite size of the oxide samples. The XRD patterns of CL and CL/A samples calcined at 773 K and 1073 K are presented in Figs. 1 and 2, respectively. For comparison purpose, the diffractograms of pure ceria (C) and γ -alumina (A) are also included. From the figures, it is clear that all samples show highly symmetric, well-defined patterns and could be indexed as (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1) and (4 2 0), which clearly manifest the peaks characteristic of the fluorite type cubic structure. No reflections from other planes related to lanthana, γ -alumina

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