CO and soot oxidation activity of doped ceria: Influence of dopants

Deboshree Mukherjee, Bolla Govinda Rao, Benjaram M. Reddy *

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

ABSTRACT

This article represents a comparative study of a series of doped ceria catalysts towards environmental applications like CO and soot oxidation catalysis. Transition and rare earth metals of varying size and reducibility property have been selected namely, zirconium (Zr), hafnium (Hf), iron (Fe), manganese (Mn), praseodymium (Pr), and lanthanum (La) as dopants. A facile coprecipitation approach has been used to incorporate the dopants into ceria lattice.The formation of homogeneous solid solutions and their respective physicochemical properties have been confirmed by employing XRD analysis, BET surface area measurements, TEM, Raman, UV-DRS, XPS, and TPR techniques. All the doped CeO_2 samples exhibited smaller crystallite size, larger BET surface area, and higher amounts of oxygen vacancies than that of pure CeO_2. CO oxidation has been performed in the presence of oxygen under atmospheric pressure, and 300–850 K temperature range in a fixed bed microreactor. Soot oxidation was carried out in presence of air using a thermo gravimetric analyzer within a much wider temperature window of 300–1273 K. The physicochemical properties of the doped ceria materials have been comparatively analyzed to correlate the influence of dopants with their improved behaviour in both the oxidation reactions. Vital role of 'lattice oxygen' in CO oxidation and 'active oxygen species' in soot oxidation on the catalyst surface has been considered, assuming that Mars and van Krevelen mechanism and active oxygen mechanism play the key role in CO and soot oxidation, respectively. The O 1s XP spectra confirmed that Mn doped ceria (denoted as CM) exhibited most loosely bound lattice oxygen and highest concentration of surface adsorbed oxygen species compared to other materials. Accordingly, a superior CO and soot oxidation activity have been observed for manganese doped ceria. Significant lowering of T_{50} (390 K and 669 K for CO and soot oxidation respectively) temperature have been observed in both the oxidation reactions; which is primarily attributed to the considerable lowering of lattice oxygen binding energy and higher concentration of surface adsorbed oxygen species.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Designing advanced doped ceria (CeO_2) materials has drawn immense research interest due to their extensive use in several environmental, energy related, and other industrial catalytic applications [1]. The importance of CeO_2 had primarily emerged from its oxygen storage capacity (OSC) and redox catalytic property [2]. Easy toggling between the oxidation states of cerium ion (Ce^{3+}/Ce^{4+}) accompanied with the formation of internal oxygen vacancies imparts excellent redox property in ceria [3]. Moreover, compared to bulk, nanoscale ceria shows outstanding catalytic activity in many applications, which is attributed to an increased specific surface area and relative ease of oxygen vacancy formation than that of the bulk material [4]. Despite its wide advantage, pure ceria

lacks some important features necessary for commercial applications. Low OSC, significant loss of active surface area due to thermal sintering, deactivation of the redox couple, reduction of catalytic activity are few among them [5–7]. Even a small degree of sintering causes a huge effect on the crystallite size and the existence of oxygen vacancies, enough to carve down the catalytic activity significantly [8]. However, presence of a foreign metal ion in the ceria lattice is well proven to strengthen its hand against thermal sintering and loss of catalytic activity, along with significant increase of OSC [9]. In addition, incorporation of dopants results in enhanced BET surface area and oxygen vacancies; thereby, reasonably improve catalytic performance even at higher temperatures [10].

The choice of a suitable dopant however, still remains a major challenge to the scientific community in terms of oxygen storage capacity, thermal stability, and economical considerations. Numerous attempts have been performed to correlate the influence of dopant features, such as oxidation state, ionic radius, electroneg-

activity, etc with the physicochemical properties and redox ability of ceria-based catalysts both from theoretical understanding and experimental observations. To mention a few, Nolan has correlated the ionic radii of trivalent dopants with the kind of defect formed on CeO_2 (110) surface from DFT+U calculations [11]. Hu et al. have illustrated the variation in oxygen vacancy formation energy in terms of valance of dopant ion from theoretical calculations [12]. Anderson et al. have correlated redox catalytic efficiency of doped material with the dopant ionic radius applying DFT calculations [13]. On the other hand, Liu et al. have illustrated a linear correlation between CO oxidation activities of doped ceria with Pauling electronegativity of the dopants from experimental observation [14]. Further, Sun et al. have demonstrated size dependent OSC of ceria nanocrystals after carrying out an in-depth analysis [15]. But combining the outcomes of those studies towards better understanding of the influence of dopant features is not straight forward. Therefore, still there exists a gap at the bottom.

Considering this fact, we have focused particularly on the correlation of physicochemical properties of doped ceria catalysts with their catalytic activity in CO and soot oxidations, which are typically performed in ceria based automobile catalysts [16–20]. CO and soot are generated due to partial burn of fossil fuel in auto mobile engine and exhibit severe effects on environment and human health [21–25]. Therefore, abatement of CO and soot has been a big concern throughout. Ceria based catalysts have been highly explored for this application from 1980s. Number of doped ceria materials have been reported to exhibit considerable activity. Lack of appropriate substitute of fossil fuel and progressively tightened emission standards have provoked more interest in this area [26–28]. Though a plenty of doped ceria catalysts are already reported to exhibit considerable activity, but their comparative study is necessary towards basic understanding of influence of dopants, which have not been well explored yet. To achieve this perception we have undertaken this comparative study and have discussed the outcomes on the basis of present observations and previous literature reports. Catalytic materials have been prepared using different class of dopant metal ions with widely varied ionic radii and reducibility, such as, zirconium (Zr), hafnium (Hf), iron (Fe), manganese (Mn), lanthanum (La), and praseodymium (Pr). Transition metals Zr and Hf have comparatively smaller ionic radii than Ce and are hardly reducible under the redox condition of ceria [20]. They are known to exist in +4 oxidation state and are capable of introducing only intrinsic oxygen vacancies. On the other hand, Mn and Fe are even smaller in size and easily reducible [7,10]. They are known to exist in multiple valance state and thereby impart extrinsic oxygen vacancy along with the intrinsic oxygen vacancies present in ceria. On the contrary, rare earth lanthanum (La) and praseodymium (Pr) exhibit higher ionic radii than Ce but Pr is easily reducible and exhibit in multiple valance state in contrary to La [19,23]. However, both of these metal ions introduce extrinsic oxygen vacancies in addition to intrinsic oxygen vacancies. Moreover, according to literature reports, La modifies the surface property of ceria which leads to formation of comparatively stable surface carbonates [19,20]. Hence, here it will be interesting to comparatively study those doped ceria materials together and analyze their physicochemical properties with their activity.

The catalysts have been prepared by choosing optimized Ce/M (M = Zr, Hf, La, Pr, Fe, Mn) mole ratio according to our previous investigations [20,29–31]. All the catalysts have been prepared via simple facile coprecipitation method under similar laboratory conditions to exclude any difference in activity caused by morphology. All the prepared materials have been calcined at 773 K and characterized using state of art techniques like X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman, UV–vis diffuse reflectance spectroscopy (UV–vis DRS), X-ray photoelectronspectroscopy (XPS). Reducibility of the prepared materials has

been investigated using temperature programmed reduction (TPR). Activity has been studied by performing CO oxidation in presence of oxygen under atmospheric pressure, 300–850 K temperature range and soot oxidation in presence of air in thermogravimetric analyzer within 300–1273 K temperature range.

2. Experimental

2.1. Catalyst preparation

The optimized solid solutions of CeO_2-ZrO_2 (CZ, 8:2), CeO_2-La_2O_3 (CL, 8:2), CeO_2-Pr_2O_3 (CP, 8:2), CeO_2-HfO_2 (CH, 8:2), CeO_2-Fe_2O_3 (CF, 9:1) and CeO_2-Mn_2O_3 (CM, 8:2) were synthesized by means of simple and economical coprecipitation method. The employed metal precursors were $Ce(NO_3)_3 \cdot 6H_2O$ (Sigma Aldrich, AR grade), $Zr(NO_3)_4 \cdot 5H_2O$ (Fluka, AR grade), $La(NO_3)_3 \cdot 6H_2O$ (Sigma Aldrich, AR grade), $Pr(NO_3)_3 \cdot 6H_2O$ (Sigma Aldrich, AR grade), $HfCl_4$ (Sigma Aldrich, AR grade), $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma Aldrich, AR grade) and $Mn(NO_3)_2 \cdot 4H_2O$ (Sigma Aldrich, AR grade) respectively. In a typical experimental procedure the requisite quantities of respective metal precursors were dissolved in distilled water separately and mixed together under efficient stirring condition. Dilute aqueous NH_3 was added as precipitating agent in drop wise manner to the above mentioned solution under vigorous stirring until it reached appropriate pH of ∼9. Afterwards, the solution was kept under stirring condition for 24 h at room temperature. The resultant precipitate was filtered off and washed several times with double distilled water, until it was free from the anionic impurities. The obtained precipitate was allowed to dry at 373 K for 12 h in electrical oven and the obtained cake was crushed in ceramic mortar in order to get fine powder. Finally, the resultant powder was calcined at 773 K for 5 h in air atmosphere at a heating of $5\,K\,min^{-1}$ to obtain the final solid solution. For comparison purpose we have also prepared pure ceria by similar procedure.

2.2. Catalyst characterization

Structural features of the prepared catalysts were studied with the help of XRD technique. XRD patterns were recorded on a Rigaku diffractometer using Cu Kα radiation (0.1540 nm), operated at 40 kV and 40 mA in the 2θ range of 2–80° with a 2θ step size of 0.02° and a time for step of 2 s. The XRD phases present in the synthesized samples were identified with the help of Powder Diffraction File-International Centre for Diffraction Data (PDF-ICDD). The average crystallite size and lattice parameters of the prepared samples were estimated using full width at half maximum (FWHM) of the most prominent X-ray diffraction peak by means of Debye-Scherer equation.

The textural properties such as surface area, pore volume, and pore size distribution of synthesized samples are determined by N_2 adsorption-desorption isotherms which are obtained using Micromeritics ASAP 2010 instrument. Prior to the analysis, the samples were evacuated at 423 K for 12 h to remove the residual moisture and flushed with argon gas for 2 h.

The transmission electron microscopy and high resolution transmission microscopy (TEM-HRTEM) studies were made on a TECNAIG2TEM microscope equipped with a slow-scan CCD camera and at an accelerating voltage of 200 kV. For the TEM analysis, few milligrams of the samples were taken and dispersed in ethyl alcohol. Further, the sample was subjected for ultra-sonication until the samples were completely dispersed in ethanol solution. After well dispersion, a droplet was deposited on a copper grid supporting a perforated carbon film and allowed to dry. The specimen was examined under vacuum at room temperature.