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Influence of isovalent and aliovalent dopants on the reactivity of cerium oxide for catalytic applications

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ABSTRACT

The influence of dopant size and valence state on the reduction properties, oxygen defects, and lattice strain in doped ceria has been studied fastidiously. This is of particular importance in environmental application, such as soot and CO oxidation. Herein, isovalent (Zr^{4+}) and aliovalent (La^{3+}, Eu^{3+}, and Sm^{3+}) metal ions doped ceria catalysts were synthesized by coprecipitation method with aqueous ammonia as the precipitant. The interplay of dopant size and valence in the ceria lattice is experimentally analysed in detail at the structural and electronic level by XRD, BET, TEM, Raman, TPR, and XPS techniques, and finally evaluated for soot and CO oxidation reactions. According to the analysis results, the size or the valence of the dopant or both together positively influence the ceria properties. The isovalent substituent (Zr^{4+}), which is different in size with respect to ceria, enhanced the ceria intrinsic activity by decreasing its reduction temperature and oxygen vacancy formation energy, thereby increased the activity. Whereas, aliovalent dopants (La^{3+}, Eu^{3+}, and Sm^{3+}) having different in size and valence compared to pure ceria further improved the structural and catalytic properties of bare ceria by inducing additional oxygen vacancies. The observed activity of doped materials towards soot and CO oxidation reactions is as follows: aliovalent doped ceria > isovalent doped ceria > ceria. The marked influence of isovalent and aliovalent dopants on the ceria properties are highlighted in this study.

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1. Introduction

From the last few decades, a number of industrial processes have increased greatly. Despite the fact that, these developments may have conspicuous benefits, the noxious gases released into the atmosphere threatening the modern civilization [1,2]. Emissions of carbon monoxide (CO), soot, NO_x, etc., have substantially increased with the use of coal, petroleum, and other related products that impact badly on our environment as well as on our health. As a result, legislation has drawn up and put constraints on gas emissions for industries. This has eventually coerced a reduction in these emissions. A series of technologies have been developed to lessen the soot and CO emissions. Among them, the primary interest is oxidation [3–5]. To date, metal oxide nanoparticles have driven increasing research efforts because of their high catalytic activity and stability [6]. Especially, nano ceria (CeO_2) catalysts for the oxidation of soot and CO possess an intrinsic advantage over other catalysts due to their momentous properties [7,8].

The main inherent property that present in ceria is buffer nature that is its ability to extract, store, and release oxygen [9–12]. With this special feature, it is used as a core material in many modern environmentally benign technologies like a promoter in three-way catalysts (TWCs) for the elimination of toxic auto exhaust gases, low temperature water-gas-shift (WGS) reaction, solid oxide fuel cells (SOFCs), solar driven thermochemical CO_2 reduction, etc. [13–17]. Furthermore, because of its structural similarity to urania and thoria, ceria is additionally used to investigate radiation damage to fuel rods in nuclear reactors [18]. Moreover, it acts as artificial oxygen modulator, which is vital to many biological processes [19]. In all these applications, researchers are constantly striving to improve the properties of ceria to obtain better performance. For this, many endeavours have been devoted to investigate the influence of doping elements on the corresponding catalytic behaviour of ceria and shown that the catalytic activity of ceria can be considerably enhanced by tuning the surface and interface structure through doping with isovalent/aliovalent cations into the ceria lattice [20–23]. The isovalent cations frequently used are (Ti^{4+}, Zr^{4+}, Hf^{4+}, Sn^{4+}, etc.) and aliovalent cations are (Mn^{2+}, Ni^{2+}, Zn^{2+}, Ca^{2+}, Mn^{3+}, Sc^{3+}, Y^{3+}, Gd^{3+}, Sm^{3+}, Eu^{3+}, La^{3+}, etc.). In these two categories, substitution of isovalent dopant into the ceria lattice decreases the

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oxygen vacancy formation energy due to the structural distortion. Whereas, in the case of aliovalent dopants the decrease in the defect formation energy is due to the structural distortion, and also due to the electronic modifications, which result in the generation of extra oxygen vacancies [24,25]. On the other hand, in aliovalent metal ions, bivalent dopants like Ca^{2+} are not preferable. Since, bivalent doped ceria materials are thermally unstable, and phase segregation occurs which makes the oxygen migration more difficult. This consideration has shrunk down to select trivalent cations as dopants in the aliovalent section to improve the ceria catalytic properties [26].

The important aliovalent metal ions that are frequently considered include La^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Sc^{3+}, etc. Among them Eu^{3+}, Sm^{3+}, and La^{3+} have important applications in various disciplines, particularly in optical, electronic devices, solid oxide fuel cells, etc. [27]. In the present study, we have selected La^{3+}, Eu^{3+}, and Sm^{3+} as aliovalent dopants and Zr^{4+} as the isovalent substituent for incorporation into the ceria lattice. These materials were prepared by a coprecipitation method and characterized by using various techniques, namely, X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area, high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, temperature programmed reduction (TPR), and X-ray photoelectron spectroscopy (XPS). Finally, we attempt to provide an overview of how the aliovalent and isovalent metal ions influence the ceria properties for catalytic applications like soot and CO oxidation reactions.

2. Experimental

2.1. Catalyst preparation

The investigated CeO_2–ZrO_2 (CZ, 1:1), CeO_2–La_2O_3 (CL, 8:2), CeO_2–Eu_2O_3 (CE, 8:2), and CeO_2–Sm_2O_3 (CS, 8:2) in different mole ratios of oxide solid solutions and a reference CeO_2 were synthesized by a modified coprecipitation method using appropriate amounts of the corresponding $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich, AR grade), $ZrO(NO_3)_2 \cdot xH_2O$ (Fluka, AR grade), $La(NO_3)_3 \cdot 6H_2O$ (Aldrich, AR grade), $Eu(NO_3)_3 \cdot 5H_2O$ (Aldrich, AR grade), and $Sm(NO_3)_3 \cdot 6H_2O$ precursors respectively. The desired amounts of the precursors were dissolved separately in double distilled water under mild stirring conditions and mixed together. Dilute aqueous ammonia solution was added drop wise over a period until the pH of the solution reached ~8.5. The resulting pale yellow coloured slurry was decanted, filtered, and washed several times with double distilled water until free from anion impurities. The obtained precipitates were oven dried at 393 K for 12 h and calcined at 773, 1073, and 1273 K for 5 h at a heating rate of 5 K min^{-1} in air atmosphere. In future, for convenience CeO_2–ZrO_2, CeO_2–La_2O_3, CeO_2–Eu_2O_3, CeO_2–Sm_2O_3, and CeO_2 are designated with CZ, CL, CE, CS, and C respectively.

2.2. Catalyst characterization

The XRD data was acquired in the 2θ range of 12–80° on a Rigaku Multiflex instrument using Cu Kα (λ = 1.5418 Å) radiation and a scintillation counter detector. Crystalline phases present in the samples were identified with the help of Powder Diffraction File-International Centre for Diffraction Data (PDF-ICDD). The average size of the crystalline domains (D) of the prepared materials was estimated with the help of the Scherrer equation (1) using the XRD data of all prominent lines.

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

where D denotes the crystallite size, λ the X-ray wavelength (1.541 Å), K the particle shape factor taken as 1, β the peak width (FWHM, full width at half maximum) in radians and θ the Bragg diffraction angle. The lattice parameter 'a' was calculated by a standard cubic indexation method using the intensity of the base peak (1 1 1). BET surface area measurements were made on a Micromeritics ASAP 2020 instrument. Prior to analysis, the samples were oven dried at 393 K for 12 h and flushed with argon gas for 2 h. The BET surface area was measured by nitrogen adsorption–desorption isotherms at liquid nitrogen temperature.

HRTEM studies were made on a JEM-2010 (JEOL) instrument equipped with a slow-scan CCD camera at an accelerating voltage of 200 kV. Raman spectra were recorded with a Horiba Jobin Yvon HR 800 Raman spectrometer at ambient temperature. The emission line at 638.2 nm from the Ar$^+$ laser (Spectra Physics) was focused on the sample under the microscope.

Reducibility of the samples was examined by TPR using thermal conductivity detector (TCD) of a gas chromatograph (Shimadzu) in a conventional apparatus. Approximately 30 mg of the sample weight was loaded in an isothermal zone of the reactor and heated at a rate of 10 K min^{-1} to 473 K using 30 mL min^{-1} He gas flow which facilitated to drive away the molecules that had been pre-adsorbed on the surface of the sample. After the sample was cooled to room temperature, then the sample was heated at a rate of 5 K min^{-1} from ambient temperature to 1073 K in a 20 mL min^{-1} flow of 5% H_2 in Ar, keeping all other parameters unchanged. 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 was analysed by gas chromatograph using TCD.

The XPS measurements were performed on a Shimadzu (ESCA 3400) spectrometer by using Al Kα (1486.7 eV) radiation as the excitation source. Charging effects of catalyst samples were corrected by using the binding energy of the adventitious carbon (C 1s) at 284.6 eV as internal reference. The XPS analysis was done at ambient temperature and pressures usually in the order of less than 10^{-8} Pa.

2.3. Catalyst evaluation

The catalysed soot oxidation was studied in a thermogravimetric analyzer (Mettler Toledo, TGA/SDTA851e). Oxidation experiments consisted of heating the soot–catalyst mixtures at 10 K min^{-1} from 300 to 1273 K in 100 mL min^{-1} flow of air. These experiments were conducted in 4–5 cycles using the same catalyst sample. No appreciable change in the soot oxidation activity was noticed. The activity measurements were performed in 'tight contact' (ground in an agate mortar) condition with catalyst–soot mixtures in 4:1 wt/wt ratio. In this experiment, the model soot used is Printex-U provided by Degussa. This soot was proven to be an appropriate model for the soot oxidation reaction.

The catalytic activity of the synthesized nanocomposite oxides was also evaluated for oxidation of CO at normal atmospheric pressure and temperatures in the range of 300–773 K in a fixed bed microreactor at a heating ramp of 5 K min^{-1}. About 100 mg catalyst sample (250–355 μm sieve fraction) diluted with quartz particles of the same sieve fraction was placed in a quartz reactor for evaluation. Temperature was measured directly at the catalyst bed using a thermocouple placed in the hollow part of the reactor. The following gases and gas mixtures were used (supplied by Air Liquide): argon (>99.999% purity), 9.98% CO in argon (CO purity, >99.997%; argon purity, >99.99%), and 10.2% O_2 in argon (oxygen purity, >99.995%). The total flow rates maintained by three mass flow controllers were in the range of 50–60 N mL min^{-1} (milliliters normalized to 273.15 K and 1 atm.). 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