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Gadolinium doped cerium oxide for soot oxidation: Influence of interfacial metal–support interactions

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ABSTRACT

The aim of the present investigation was to ascertain the role of Al_2O_3, SiO_2, and TiO_2 supports in modulating the catalytic performance of ceria-based solid solutions. In this study, we prepared nanosized Ce-Gd/Al_2O_3, Ce-Gd/SiO_2, and Ce-Gd/TiO_2 catalysts by a deposition coprecipitation method and evaluated for soot oxidation. The synthesized catalysts were calcined at two different temperatures to assess their thermal stability and extensively characterized by various techniques, namely, XRD, Raman, BET surface area, TEM, H_2-TPR, and UV–vis DRS. XRD and TEM results indicate that Ce-Gd-oxide nanoparticles are in highly dispersed form on the surface of the supports. Raman results show a prominent sharp peak and a broad peak corresponding to the F_{2g} mode of ceria and the presence of oxygen vacancies, respectively. The presence of a significant number of oxygen vacancies in all samples is also confirmed from UV–vis DRS measurements. The H_2-TPR results suggest that Gd-doping facilitates the reduction of the materials and decreases the onset temperature of reduction. Among the prepared samples, Ce-Gd/TiO_2 catalyst exhibited the highest activity, suggesting the existence of strong interfacial metal support interaction between the active metal oxide and the support.

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1. Introduction

Diesel engines are becoming more prominent nowadays because they are more fuel-efficient compared to gasoline engines. However, they present the environmental drawback of soot (particulate matter) emission as one of the main pollutants together with small amounts of NO_x, CO, and unburned hydrocarbons [1,2]. With growing concerns of health effects associated with diesel soot (these particles are suspected to the development of cancer, cardiovascular, and respiratory health effects) and its influence on the earth's climate (pollution of air, water, and soil), there is an increasing demand to develop technologies for controlling the emissions from stationary and mobile sources, and to make diesel engines environmental friendly [3–5]. An elegant solution to this problem is the use of a trap that performs both, removal of the soot from the exhaust stream by filtration and its subsequent catalytic combustion [6]. In diesel exhaust emissions, two oxidizing gases (oxygen and nitrogen dioxide) are generally present. Both are suitable for the oxidation of soot. Thus, the reactivity of soot towards these gases represents the main issue for an efficient regeneration of

the trap [7,8]. However, oxidation of diesel engine exhaust gas to CO_2 in uncatalyzed soot filter generally requires high temperature, which is uncontrolled and inefficient. Hence, the key challenge is to develop catalysts which produce highly reactive oxygen species from O_2 molecules facilitating high catalytic activity at much lower temperatures [9,10].

In order to promote the oxidation of soot in diesel particulate filter (DPF) many efforts have been undertaken to develop active and stable catalysts. An additional aim is to minimize or even completely substitute the use of noble metals in these applications. The use of noble metals is restricted by their high cost, limited availability, and their sensitivity to sulphur poisoning made necessary to find out appropriate alternatives [11,12]. Recently, much attention has been given to nanosized cerium dioxide (nano-CeO_2) because it exhibits a high level of catalytic activity as a diesel fuel additive. It increases fuel efficiency by enhancing the combustion of soot by improving fuel burn and by reducing the ignition temperature. It is well-known that, the catalytic properties of ceria are connected to its ability to undergo easy, fast, and reversible reduction to sub-stoichiometric phases (CeO_2–CeO_{2-x}). These unique redox properties combined with the high oxygen storage capacity (OSC) allow ceria to catalyze soot oxidation even without the participation of NO_x [6,13]. Oxygen vacancies play an important role in this reaction since they are responsible for the

adsorption–desorption properties of the reactants and facilitate the diffusion of lattice oxygen from the bulk to the surface. That would lead to the enhancement of the catalytic activity [14].

Nevertheless, pure ceria does not satisfactorily fulfil the elevated activity demands owing to its deactivation of the redox couple and insufficient thermal stability [15]. Hence, many efforts have been made to prepare CeO_2-based materials with improved electronic properties and thermal stability. Modification of the structure by doping as well as its dispersion on the surface of another metal oxide support represents one of the successfully adopted routes [16–18]. Rodriguez et al. [19] demonstrated that strong metal–support interactions induce significant changes in the electronic and chemical properties of the sites on the metal particle's surface to achieve better catalytic activity. Similarly, the catalytic activity of metals dispersed on a support is influenced by many factors such as the relative amount of metal present, its extent of dispersion, the chemical nature of the support, and the strength of the interaction between the support and the metal [20]. It is observed that different oxide supports, such as Al_2O_3, SiO_2, and TiO_2 enhance the formation of active oxygen species in CeO_2 due to their synergistic interaction with the dispersed ceria. These supports are considered as thermally stable with reasonably good chemical stability and low cost. γ-Al_2O_3 supported ceria-based materials have been extensively used and proven to be the most advanced materials for three-way catalysis (TWCs) [21]. It has been observed that supporting ceria on silica enhances its catalytic activity, which combined with the stability of silica at high temperatures and the abundance of micro-pores and meso-pores represent a very promising way to explore [22]. TiO_2 is a well-known catalyst in environmental applications and also serves as an active support for the oxidation of soot [23]. In general, catalytic soot combustion is affected by two factors: the contact condition between soot and the catalyst, and the intrinsic activity of catalyst. The intrinsic activity (oxygen vacancy concentration and concomitant oxide ion conductivity in cerium oxide) of the catalyst could be enhanced by homogeneously doping of ceria with an appropriate transition (Fe, Co, etc.) or rate-earth metal cation (La, Sm, Eu, Gd, etc.), which improves the oxidation activity of the catalyst. This modification has often been attributed to changes in the redox properties and the creation of oxygen vacancies. The lower-valent rare earth cation like Gd^{3+} is found to form substitutional solid solution with ceria. The Ce-Gd solid solution is proposed for intermediate temperature application of solid oxide fuel cells with high ionic conductivity. Oxygen vacancies are generated for substitution of every two Ce^{4+} ions by two Gd^{3+} ions in order to maintain the charge neutrality mechanism and can introduce extrinsic oxygen vacancies. These result in a higher mobility of lattice oxygen and allow transporting oxygen species from the surface to the bulk and vice versa which contributes to lower the oxidation temperature [24–26].

Based on the above observations, our main objective of the present work was to perform an experimental study to determine the role of supports on ceria-based materials for soot oxidation. For this purpose, we have synthesized stable gadolinium doped CeO_2 catalysts supported on different oxides namely, Al_2O_3, SiO_2, and TiO_2 to produce extrinsic oxygen vacancies for soot oxidation in the presence of air. The redox cycle of ceria ($Ce^{4+} \leftrightarrow Ce^{3+}$) confers the ability to adsorb gaseous O_2, thus forming active oxygen species at the catalyst surface. These can be transferred to the soot–catalyst interface by surface diffusion [27]. For an efficient synthesis of Ce-Gd/Al_2O_3, Ce-Gd/SiO_2, and Ce-Gd/TiO_2 catalysts, we have devised a simple and convenient strategy based on an aqueous deposition-precipitation method. The synthesized catalysts were extensively characterized by various techniques, namely, X-ray diffraction (XRD), transition electron microscopy (TEM), visible-Raman spectroscopy (vis-RS), N_2 adsorption–desorption isotherms, UV–vis diffuse reflectance spectroscopy (UV–vis DRS),

and temperature programmed reduction with hydrogen (H_2-TPR). The unique properties and the metal oxide support interaction between CeO_2-Gd_2O_3 and Al_2O_3, SiO_2, and TiO_2 are interpreted in terms of structural information derived from physicochemical analysis.

2. Experimental

2.1. Materials and methods

The nanosized cerium-gadolinium oxide solid solutions on Al_2O_3, SiO_2, and TiO_2 supports (support:CeO_2:Gd_2O_3 = 100:80:20 mol% based on oxide) were synthesized by a deposition coprecipitation method using dilute aqueous ammonia solution as the precipitating agent. The precursors employed were $Gd(NO_3)_3$·$6H_2O$ (99.9% purity), and $Ce(NO_3)_3$·$6H_2O$ (99.5% purity), γ-Al_2O_3 (commercial, surface area 208 $m^2\,g^{-1}$), colloidal SiO_2 (Ludox, 40 wt.%, Aldrich,) and TiO_2-anatase (EU consortium, surface area 49 $m^2\,g^{-1}$), respectively. First, cerium and gadolinium nitrates were dissolved separately in deionized water and mixed in appropriate quantities. The supporting oxides were dispersed separately in deionized water by vigorous stirring and then added to the cerium-gadolinium precursor solution. The mixture was diluted with deionized water and stirred for an additional hour. To precipitate the gadolinium and cerium hydroxides, aqueous NH_3 solution was added drop-wise to the mixture under vigorous stirring until the pH reached ~10.5. After filtration, the cake was dried at 120 °C for 12 h. Then, the dried cake was ground and calcined at 500 °C for 5 h in air. Parts of the 500 °C calcined sample were further treated at 800 °C for 5 h in air atmosphere to compare the stability and activity. Hereafter, the composite oxides will be referred as Ce-Gd/Ax, Ce-Gd/Sx, and Ce-Gd/Tx (where Ce, Gd, A, S and T stand for CeO_2, Gd_2O_3, Al_2O_3, SiO_2 and TiO_2 respectively and x represents the calcination temperature, 500 and 800 °C).

2.2. Catalyst characterization

Structural features of the catalysts were characterized by XRD. The XRD patterns were recorded on a Philips X'Pert diffractometer operated at 40 kV and 40 mA using nickel filtered Cu Kα radiation (λ = 0.15418 nm). Diffraction patterns were recorded in the range 2° < 2θ < 80° with a step size of 0.02° and an integration time per step of 1 s. The Philips X'Pert HighScore software was used for phase identification. The mean crystallite size was estimated from the full width at half maximum (FWHM) of the X-ray diffraction peaks using the Scherrer equation with a correction for instrument line broadening [17]. The textural properties of the prepared samples were determined by a single point N_2 adsorption–desorption isotherms at liquid N_2 temperature (−196 °C) using a Micromeritics Tristar apparatus with Micromeritics VacPrep 061 sample degas system. Specific surface areas were calculated by Brunauer–Emmett–Teller (BET) method. Prior to the measurements, the samples were evacuated at 150 °C for 6 h to remove any residual moisture. Raman spectra were recorded at ambient temperature and pressure on a DILOR XY spectrometer equipped with liquid nitrogen cooled CCD detector. The emission line at 632.81 nm from an Ar^+ ion laser was focused on the sample under the microscope. Accuracy of the wavenumber calibration is ±1 cm^{-1}. The acquisition time was adjusted for each sample individually depending on the scattering intensity of the specific sample. TEM measurements were performed on a JEOL JEM 2010 microscope equipped with a LaB$_6$ cathode and with high-tilt objective lenses. The acceleration voltage was set to 200 kV. For these studies, a suspension of the sample in ethanol was placed in an ultrasound bath and then a drop of it