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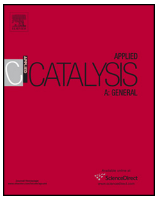

Nanostructured $Ce_{0.7}Mn_{0.3}O_{2-\delta}$ and $Ce_{0.7}Fe_{0.3}O_{2-\delta}$ solid solutions for diesel soot oxidation

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ABSTRACT

Nanostructured $Ce_{0.7}Mn_{0.3}O_{2-\delta}$ (CM) and $Ce_{0.7}Fe_{0.3}O_{2-\delta}$ (CF) solid solutions were prepared by a facile coprecipitation method and evaluated for soot oxidation. The structural, morphological, and surface properties were investigated by various techniques, namely, XRD, ICP-OES, BET surface area, SEM-EDX, TEM-HRTEM, UV–vis DRS, Raman, FT-IR, XPS, H_2-TPR, and TGA-DTA. XRD and TEM results confirmed formation of nanocrystalline solid solutions with the incorporated Mn and/or Fe cations in the ceria lattice. SEM studies ensured nanoparticle nature of Ce–Mn–O and Ce–Fe–O solid solutions with homogeneous distribution. ICP-OES and EDX analysis confirmed actual amount of metal loadings in the respective catalysts. UV–vis DRS and Raman results revealed the formation of more oxygen vacancies, which lead to the creation of more surface active species (Ce^{4+}/Ce^{3+} and O^*). XPS results revealed that the doping of Mn and/or Fe into the ceria lattice makes some Ce^{4+} transferred into Ce^{3+} in order to maintain the electrical neutrality, thereby facilitate the reduction of $Ce^{4+} \rightarrow Ce^{3+}$ and the formation of oxygen vacancies. TPR results showed that the mixed oxides reduce at lower temperatures than pure ceria. This observation confirmed that there is a synergetic interaction between Ce–O and M–O (M = Mn, Fe). The catalytic activity of CM and CF samples towards soot oxidation has been evaluated under tight contact conditions and compared with the well-established CeO_2–ZrO_2 (CZ) catalyst. Among the investigated catalysts, the Mn and/or Fe doped ceria solid solutions showed improved catalytic activity. The order of activity is as follows: CM > CF > CZ > C. Further, the CM and CF catalysts were found to be thermally quite stable compared to pure ceria. In particular, the CM sample exhibited superior catalytic activity ($T_{50} = \sim 665$ K) and thermal stability towards soot oxidation.

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1. Introduction

Currently, the diesel-powered engines are prevalent power sources for vehicles compared to gasoline-powered engines due to their superior fuel economy, low-operating cost, high durability, and reliability [1]. They are expected to play a major role in the prevention of global warming by increasing fuel efficiency, thereby lowering the CO_2 emissions. Despite their few advantages, the incomplete combustion in diesel engines leads to hazardous pollutants such as nitrogen oxides (NO_x), particulate matter (PM), and a fewer amounts of CO and unburned hydrocarbons [2]. Among them, PM also often simply called as soot, has a significant impact on human health and environment due to its potential mutagenic and carcinogenic activity. For example, the extremely small size (<1 μm) of soot particles poses tremendous harm to human health associated with the respiratory system, lung cancer, cardiovascular, and allergic diseases [3]. These issues have triggered significant research efforts in the development of novel strategies to mitigate soot emissions. Therefore, the control of soot emission has become one of the focal research topics in the field of environmental catalysis. There are several solutions relying on suitable after-treatment technologies and among them, the most effective and widely applied technology for PM control is based on the diesel particulate filter (DPF) [4]. However, a major problem concomitant with this approach is the difficulty in filter regeneration, because high temperatures (~873 K) are required to accomplish soot combustion [5]. Alternatively, the most promising method to nullify soot emissions is to capture them in a filter with the subsequent catalytic oxidation [6]. Currently, supported noble metal catalysts such as platinum are employed which exhibit an excellent catalytic activity, but suffer from several drawbacks such as sensitivity to sulfur poisoning, limited abundance, and impact on the environment [7]. Hence,

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several attempts were made to develop potential substitute catalysts for soot combustion based on simple metal oxides/mixed oxides since they are inexpensive and exhibit high resistance to poisoning [8–10].

Several authors pointed out the importance of redox properties of the metal oxides towards soot oxidation because the soot combustion is a kind of deep oxidation reaction [11]. A large number of metal oxides such as ZrO_2, TiO_2, SiO_2, Al_2O_3, and CeO_2 have been extensively investigated for the catalytic combustion of diesel soot [11,12]. Among them, ceria (CeO_2) has attracted continuous interest owing to its unique combination of an elevated oxygen transport capacity coupled with the ability to shift easily between reduced and oxidized states ($Ce^{3+} \leftrightarrow Ce^{4+}$) [7]. Due to these features, it is exploited as a major catalytic component in many after treatment technologies. For instance, Bueno-López et al. explained that the active oxygen on the surface of CeO_2 is a determining factor for soot oxidation due to its efficient oxygen buffer capacity [13]. Additionally, ceria could retain its fluorite crystal structure even after the lattice oxygen is removed with the consequent formation of a large number of oxygen vacancies. However, ceria alone as a catalyst is not appropriate for direct applications because of significant deactivation of the redox couple when subjected to thermal treatment in the driving conditions [14]. Even a small degree of sintering has a large effect on the presence of oxygen vacancies and crystallite size [15].

In the recent studies it was found that the incorporation of aliovalent/isovalent metal cations into the lattice of CeO_2 confers unusual properties due to the creation of structural defects and acceleration of oxygen diffusion in the bulk [16]. Particularly, the doping of CeO_2 with transition metals is prominent because they exhibit several oxidation states and better redox properties than rare-earth metals [17]. Additionally, the size of substituent is also one of the exceptional factors to increase the reducibility and oxygen storage capacity (OSC) of ceria [18]. The substitution of cation with the smaller ionic radius than the Ce cation can create both short and long range M–O bonds. Apparently, the oxygen atoms bonded to the metal with long range could be weaker, thus increase the reducibility of ceria. Therefore, the strong oxidative property of transition metals in combination with the oxygen storage property of ceria makes transition metal-ceria mixed oxide catalysts as a group of cheap and efficient candidate catalysts for soot oxidation [19]. Indirectly, ceria can also play vital role as a structural and chemical promoter to improve the activity and stability of transition metal catalysts. It is well reported in the literature that the catalytic activity for soot combustion of CeO_2 can be significantly improved by Zr^{4+} doping [12]. The doping enhances the thermal stability of CeO_2 as well as increased catalytic activity with regard to bare ceria after thermal deactivation [20]. Apart from ZrO_2, the MnO_x and FeO_x were particularly fascinating as ecofriendly catalysts for the abatement of contaminants since they usually have different oxidation states and exhibit excellent redox properties [21]. Furthermore, the synergistic effect would be anticipated from the combination of these metal oxides with CeO_2. As mentioned earlier, the strong interaction of ceria with transition metal oxides MO_x (M = Mn, Fe) could deteriorate the M–O bond, which is favourable for various catalytic applications such as water gas shift reaction, CO and soot oxidation, and other [22]. Therefore, the importance of OSC and redox property towards various applications in catalysis instigate us to investigate the effect of structural features of Ce–M (M = Mn, Fe) mixed oxides towards soot oxidation. Accordingly, the mixed oxide catalysts CeO_2–MO_x (M = Mn, Fe) were synthesized by a coprecipitation method. The structural properties, redox behaviour and catalytic performance of the prepared catalysts for soot oxidation were carefully investigated and correlated.

2. Experimental

2.1. Materials and methods

The optimized nanocomposite $Ce_{1-x}M_xO_{2-\delta}$ (M = Mn, Fe; 70:30 mol% based on oxides) solid solutions were synthesized by a coprecipitation method. In order to prepare $Ce_{0.7}Mn_{0.3}O_{2-\delta}$, the desired amounts of $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich, AR grade) and $Mn(NO_3)_2 \cdot 4H_2O$ (Merck, AR grade) precursors were dissolved separately in distilled water and mixed together under stirring conditions. Dilute aqueous ammonia was added dropwise gradually to the aforementioned mixture solution with vigorous stirring, until precipitation was complete (pH = ~8.5) and the stirring was continuing constantly for 24 h. After that, the precursor precipitate was separated from the supernatant by vacuum filtration and several times thoroughly washed with distilled water until free from impurities. The obtained precipitate was then dried in an electrical oven at 373 K for 12 h, crushed for 10 min in order to make a fine powder using ceramic mortar. Finally, the powder was calcined for 5 h (the heating and cooling rates were in the steps of 5 K min^{-1}) in a closed electric furnace at 773 K to obtain the mixed oxide and it was designated as CM. The similar method was followed to prepare $Ce_{0.7}Fe_{0.3}O_{2-\delta}$ using Ce and Fe nitrate precursors and it was designated as CF. In order to understand the thermal effect on the catalytic activity, the mixed oxides were calcined at 1073 K for 5 h. For comparison purpose, a pure ceria sample was also prepared under identical conditions using cerium nitrate as the precursor and represented as C.

2.2. Catalyst characterization

X-ray powder diffraction patterns were acquired on an X'pert Pro MPD powder diffractometer (PANAlytical Company) equipped with a nickel-filtered Cu Kα (0.15418 nm) radiation source and a scintillation counter detector (SCD). The scattered intensity data were collected from 2θ values of 2–80° by scanning at 0.01° steps with a counting time of 1 s at each step. Crystalline phases were identified by matching with the International Centre for Diffraction Data Powder Diffraction File (ICDD-PDF). The average crystallite size (D) of the samples was determined with the help of Scherrer equation from line broadening and the lattice parameters (a) were estimated through the formulae $a = (h^2 + k^2 + l^2)^{1/2} \times (\lambda/2\sin\theta)$ using the intensity of the most prominent peak (1 1 1).

The chemical analysis of the prepared samples was performed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Jarrel Ash model IRIS Intrepid II XDL, USA) to confirm the respective concentrations of elements in the system. For ICP analysis, approximately 50 mg of the sample was dissolved in a solution of 25 ml aqua regia and 475 ml distilled water. Then 10 ml of the above solution was diluted to 250 ml.

The surface area and pore size distribution of the as-prepared samples were determined by N_2 adsorption–desorption isotherms at liquid N_2 temperature (77 K) on a Micromeritics (ASAP 2000) analyzer. Specific surface area and pore size distribution were calculated by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. Prior to the measurements, the samples were pre-treated in a vacuum oven at 473 K for 2 h to remove any residual moisture.

SEM studies were performed by using a Zeiss EVO® series electron microscope to examine surface morphology, and the energy dispersive X-ray analysis (EDX) was used to determine the elemental composition of samples. The scanning electron microscope was equipped with a LaB_6 source and an EDAX/DX4 detector. The acceleration potential voltage was maintained at 15 kV and samples were metallized with gold.

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