

Rational Design of Ceria-Based Nano-Oxides for Improved Catalytic Activity

THESIS

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The ever growing energy demand and the resulting stress on the Mother Nature urged to develop efficient catalytic materials towards environment related applications and generation of clean energy. Ceria (CeO_2) is one of the most important rare earth oxides, which found important applications in the field of catalysis for commercial purposes, typically including, three-way catalysts (TWC) for the elimination of toxic automobile emissions, environmental protection and remediation (wet-oxidation of organic pollutants in water, elemental mercury abatement, etc.), solid oxide fuel cells (SOFCs), solar driven thermochemical CO_2 reduction and H_2 production, low-temperature water-gas shift (WGS) reaction, selective oxidation reactions, biomass reforming, medical sciences, *etc.* The most attractive property of CeO_2 is its oxygen storage capacity (OSC) which renders it a suitable candidate for catalytic applications. CeO_2 can store and release oxygen reversibly with an easy switch between +4 and +3 oxidation states of Ce under oxidizing and reducing conditions, respectively. Due to the larger ionic radius of Ce^{3+} ion (1.14 Å) compared to Ce^{4+} ion (0.97 Å), the surrounding fluorite lattice distorts during the formation of O vacancies and Ce^{3+} defect centers resulting in enhancement of oxide ion mobility in the lattice. Other advantageous features of CeO_2 include its high mechanical strength, oxygen ion conductivity, nontoxic nature, *etc.* Despite of all these favorable features, pure CeO_2 faces some serious drawbacks. At high temperature CeO_2 undergoes rapid sintering leading to loss of oxygen storage capacity and reduction of catalytic activity. Moreover, the amount of oxygen supplied during redox reactions is relatively less, which makes pure CeO_2 unsuitable for practical applications. Doping of appropriate foreign metal cations into CeO_2 lattice improves its structural stability and redox catalytic activity. Further, reducing the particle size to nano-scale and increasing the surface area is a nice strategy to enhance the surface reactive sites with respect to the bulk of the material. Doped nano-ceria based materials exhibit smaller crystallite size, higher surface area, abundant oxygen vacancies, and superior redox properties compared to pristine ceria.

However, choosing a suitable dopant metal ion is a tricky task, as the incorporated dopant ions influence the physicochemical properties and catalytic activity in different ways. A thorough literature search shows a number of interesting publications in relation

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with the improvement of catalytic properties of CeO_2 by use of dopants. However, those isolated reports do not lead towards a straightforward answer of the obvious question that ‘how to choose a suitable dopant?’.

Against the aforementioned background a comparative study was undertaken with a series of doped CeO_2 materials. A number of dopants were selected from transition and rare earth metal family. Mixed oxides of CeO_2 and dopant oxides were prepared by co-precipitation method. The experimental conditions were strictly maintained the same during materials’ preparation. The physicochemical properties were studied at length using various state-of-the-art techniques. The catalytic activity of the prepared materials were assessed by carrying out carbon monoxide and diesel soot oxidation, the two important steps in catalytic elimination of harmful automobile exhaust. The physicochemical properties of the prepared materials were corroborated with the catalytic activity, which helped us to look for the desirable properties in dopants. Among the dopants tested in this experiment, manganese (Mn^{x+}) doped CeO_2 showed the best catalytic activity in CO and soot oxidation.

Further the Influence of support materials were tested with the best performing Mn doped CeO_2 ($\text{CeO}_2\text{-MnO}_x$) catalyst. Usually, a very strong interaction between the support and active phase hinders the electron transfer process affecting the catalytic activity. On the contrary, too weak interactions permit migration of the supported particles on the support surface resulting in sintering and decrease of active surface area. In this investigation, the influence of anatase- TiO_2 and $\gamma\text{-Al}_2\text{O}_3$ supports were tested and compared with unsupported $\text{CeO}_2\text{-MnO}_x$ mixed oxide catalyst in soot oxidation catalysis. The catalytic activity of the samples were found to follow the order of $\text{CeO}_2\text{-MnO}_x/\text{TiO}_2 > \text{CeO}_2\text{-MnO}_x/\text{Al}_2\text{O}_3 > \text{CeO}_2\text{-MnO}_x$. The better activity of TiO_2 supported sample over the Al_2O_3 supported $\text{CeO}_2\text{-MnO}_x$ was accredited to the beneficial role of $\text{CeO}_2/\text{TiO}_2$ interface in creation of defect sites.

The next investigation included a thorough study of tin (Sn^{x+}) doped CeO_2 promoted with CoO_x for diesel soot oxidation catalysis. The prepared materials were systematically characterized. In the $\text{CoO}_x/\text{CeO}_2\text{-SnO}_x$ hybrid catalyst CoO_x was

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confirmed to be Co_3O_4 . HRTEM images depicted the presence of stepped catalyst surface, which has a special importance in enhancing the heterogeneous catalytic reaction rate carried out on the solid catalyst surface. Model soot was combusted in the presence of air under both tight and loose contact condition of the catalyst and soot. The hybrid catalyst exhibited improved performance compared to Sn-doped nano- CeO_2 and Co_3O_4 promoted nano- CeO_2 catalysts. The improved catalytic activity was attributed to the existence of synergism among the multivalent cations of Ce, Sn and Co. Moreover, the stepped surface of the hybrid catalyst with attached active oxygen acted as the potential active sites for the oxidation catalysis.

Raman spectroscopic investigation of the role of dopants in incorporating bulk and surface defects in CeO_2 and enhancing the OSC was carried out in the next experiment. Dopants of CeO_2 for this study were selected from the rare earth group of metals. The materials were prepared by coprecipitation method and subsequently characterized. The Ce 4f – O 2p band gap of the doped CeO_2 materials were evaluated employing Kubelka-Munk function. Generation of bulk defects give rise to an intermediate electronic state which leads to narrowing of the Ce 4f – O 2p band gap. In the present study decrease of band gap energy in the doped CeO_2 samples provided a direct proof of defect concentration enhancement in the doped materials. A direct correlation was found among the concentration of bulk defect and OSC of the prepared materials. Finally, CO oxidation reaction was performed with the catalytic materials and the activity was in accordance with the enhancement of defect concentration and OSC.

In the next investigation efforts were made to find the promotional effect of CeO_2 in the upgradation of bio-oil to biofuel. Vanillin was chosen as the model compound of bio-oil for upgradation to bio-fuel through hydrodeoxygenation using gaseous H_2 . A series of mono-, bi-metallic catalysts with and without CeO_2 promoter and SiO_2 support were prepared, systematically characterized, and subjected to hydrodeoxygenation of vanillin under optimized conditions. The CeO_2 promoted Cu-Ni (Cu:Ni=1:1) bimetallic catalyst supported on SiO_2 showed excellent activity and selectivity for the mentioned application. The promotional effect of CeO_2 was understandable from the synergistic interaction of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ with the $\text{Cu}^{2+}/\text{Cu}^{+1}$ redox couple, which directly interacts

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with the aldehyde group of vanillin during the hydrodeoxygenation process. Moreover, use of SiO₂ support significantly enhanced the surface area and improved the catalytic activity.

The experimental details of the mentioned studies along with the vital observations and results obtained are summarized in the present thesis in five consecutive chapters as briefed below-

Chapter 1 comprised of a thorough literature survey on nanostructured metal oxides with special emphasis on cerium oxide and its composite oxides. Structural, redox properties and potential applications of CeO₂ in catalysis are presented with relevant references. A brief account of the application of nanostructured metal oxides to different catalytic processes is also included. Importance of catalyst supports and promoters has been discussed at length in this chapter. The main objectives and the scope of the present thesis are also clearly outlined.

Chapter 2 describes the synthetic methods, characterization techniques, and catalytic applications employed in this investigation. The details of preparative methodologies used to obtain various ceria based materials are presented with appropriate references. The experimental details related to XRD, ICP-OES, BET SA, SEM-EDX, TEM-HRTEM, RS, SEM-EDX/EDS, UV-DRS, XPS, TPR and TGA/DTA are given with necessary theoretical background. The experimental aspects of the oxidation of CO and soot, selective hydrodeoxygenation of vanillin are also described in this chapter.

Chapter 3A deals with the influence of a series of isovalent and aliovalent dopants (CeO₂-MO_x, ; M, selected from rare earth and transition metals groups) on the physicochemical properties of CeO₂ and oxidation catalysis of carbon monoxide and diesel soot. The nanostructured catalysts were prepared by a simple, facile, high yielding co-precipitation method and calcined at 773 K. The physicochemical characterization was performed by using various techniques. The XRD results confirmed the formation of nanocrystalline single phase CeO₂-MO_x (CM) solid solutions. The aliovalent metal ions incorporated intrinsic oxygen vacancy along with extrinsic vacancies, resulting in higher oxygen storage capacity. The H₂-TPR studies evidenced the lowest temperature of reduction

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for the manganese (Mn) doped CeO₂ sample (CeO₂-Mn₂O₃) among the samples investigated. Addition of Mn dopant remarkably enhanced the OSC, reducibility and catalytic efficiency of CeO₂. This enhanced OSC was attributed to the higher amount of oxygen vacancies and Ce³⁺ ions found on the CeO₂-Mn₂O₃ surface. O 1s XPS of CeO₂-Mn₂O₃ revealed a noticeably low binding energy of lattice oxygen, which may be attributed to the disparity of electronegativity between host and dopant ions. The loosely bound lattice oxygen promoted the CO oxidation catalytic activity. Moreover, the concentration of surface adsorbed O species was also higher in CeO₂-Mn₂O₃ compared to other materials, which could be held responsible for considerably low temperature of soot oxidation activity. Higher degree of lattice strain exhibited in CeO₂-Mn₂O₃, which can be accredited for the increase of oxygen mobility from bulk to surface. Furthermore, Mn XPS indicated presence of multiple oxidation states in CeO₂-Mn₂O₃. Hence, presence of synergistic interaction between Ce and Mn redox couples could be expected, which promoted the redox catalytic activity of ceria in turn. All these factors together contributed in promoting the physicochemical properties of manganese doped ceria towards enhancement of oxygen storage property and redox catalytic activity for CO and soot oxidation.

Chapter 3B demonstrates an investigation on the influence of support materials over the reducibility and catalytic activity of CeO₂-Mn₂O₃, which was the best performing catalyst in the previous experiment. γ -Al₂O₃ and anatase- TiO₂ were used as support materials in this work. The anatase-TiO₂ and γ -Al₂O₃ supported CeO₂-Mn₂O₃ were studied in comparison to unsupported CeO₂-Mn₂O₃ mixed oxide for soot oxidation catalysis. The unsupported and anatase-TiO₂, γ -Al₂O₃ supported ceria-manganese mixed oxide solid solutions were prepared by coprecipitation and disposition-coprecipitation methods, respectively and characterized. Formation of bulk defects and surface defects were examined using the Raman and XP spectroscopy. The bulk defect concentration was correlated with the band gap energy values obtained using Kubelka-Munk function. O₂-TPD and H₂-TPR studies evidenced the improved redox capacity of the TiO₂ supported catalyst. The interaction of anatase-TiO₂ support with the active phase also imparted considerable stability, which resisted the high temperature annealing treatment. The catalytic activity of the samples were found to follow the order of CeO₂-Mn₂O₃/TiO₂ > CeO₂-Mn₂O₃/Al₂O₃ > CeO₂-Mn₂O₃. The better activity of CeO₂-Mn₂O₃/TiO₂ over

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CeO₂-Mn₂O₃/Al₂O₃ was in conflict to the BET surface area values of the respective catalysts. However, the beneficial role of the CeO₂/TiO₂ interface in creation of defect sites was apparent from the estimated higher bulk defect concentration and lower band gap energy values of CeO₂-Mn₂O₃/TiO₂. The most important observation was the sudden rise of O₂ desorption above 500 K temperature, which could be attributed to the enhancement of ionic mobility at elevated temperature as well as the availability of more defect sites in the bulk. In good accordance, the soot conversion profile of CeO₂-Mn₂O₃/TiO₂ evidenced a steep rise after ~550 K. In the present study, an optimal interaction between the TiO₂ support and CeO₂-Mn₂O₃ solid solution was apparent, which improved the structural stability and allowed favorable exploitation of unique promotional properties of CeO₂/TiO₂ interface in creation and stabilization of defect sites. Substantial stability in structural features and catalytic activity were retained even after high temperature annealing treatment.

Chapter 4A deals with the synthesis and characterization of nano-Co₃O₄ promoted CeO₂-SnO_x hybrid catalyst (Co₃O₄/CeO₂-SnO₂). In this study, pure CeO₂, SnO₂ doped CeO₂, CoO_x promoted CeO₂, and Co₃O₄ promoted CeO₂-SnO₂ samples were prepared by precipitation and deposition coprecipitation methods and characterized. The diesel soot oxidation activity of all the prepared materials was evaluated for model soot oxidation under the tight and loose contact of catalyst and soot. The corresponding results were compared and corroborated with the characterization results. The co-presence of Sn dopant in CeO₂ lattice and dispersed Co₃O₄ promoter on the catalyst surface remarkably improved the catalytic efficiency compared to CeO₂-SnO₂ mixed oxide and Co₃O₄ promoted CeO₂. The XRD and Raman results established the presence of dispersed Co₃O₄ phase and cubic fluorite nature of the CeO₂-SnO₂ mixed oxide in the Co₃O₄/CeO₂-SnO₂ catalyst. Multiple valance states of Ce, Sn, and Co were detected from XP spectra. This resulted in a synergistic interaction between the redox couples of the different metal cations present on the catalyst surface and led to superior redox catalytic activity of Co₃O₄/CeO₂-SnO₂. Moreover, the HRTEM images displayed edged/stepped surface. A higher relative density of the surface adsorbed oxygen species was identified on the stepped surface of Co₃O₄/CeO₂-SnO₂ catalyst. The higher amount of surface

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adsorbed oxygen species actively participated in the soot oxidation, resulting in a promotional effect on the catalytic activity. The promotional effect of Sn dopant and Co_3O_4 promoter was also observed in the soot oxidation under loose contact of catalyst and soot.

Chapter 4B deals with the visible Raman spectroscopic investigation of bulk defect features of doped ceria-based materials in correlation to their reducibility and redox catalytic activity. Creation of bulk defects narrow down the O 2p and Ce 4f band gap by generation of intermediate state. Thus, decrease of band gap energy provides a direct evidence of increase of defect concentration in ceria. The present investigation has utilized Kubelka-Munk function to determine the direct band gap energy of the materials under the study. OSC of the materials under investigation was determined by TG method, which has been correlated with defect concentration. Lanthanum (La) and samarium (Sm) were chosen as dopants of CeO_2 . The materials were prepared by simple and facile coprecipitation method. Formation of solid solutions was established through X-ray diffraction, transmission electron microscopy, and high resolution transmission electron microscopy studies. X-ray photoelectron spectroscopy was employed to detect the surface properties of the samples. Finally, CO oxidation reaction was performed to examine the redox catalytic efficiency of the materials. The F_{2g} peak of the Raman spectra were shifted in the doped samples, which was attributed to the change of lattice parameter due to substitution of the Ce^{4+} ion with dopant cations Sm^{3+} and La^{3+} . Broadening of the peak was also observed, which could be ascribed to smaller crystallite size of the prepared materials. Appearance of the additional peak (D_1) at $\sim 560 \text{ cm}^{-1}$ was accredited to the formation of oxygen vacancy defects. The ratio of the intensity of the D_1 to F_{2g} peak gave an approximate idea about the defect concentration of the prepared materials. Higher defect concentration was found for the samarium doped ceria. Moreover, lower O 2p \rightarrow Ce 4f band gap energy of the samarium doped ceria indicated presence of higher amount of lattice defects. OSC was also higher in ceria-samarium. CO oxidation study showed lower light off temperature for the samarium doped ceria sample, which was in agreement with the increased OSC and defect concentration of the material.

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Enhanced surface area and loosely bound surface oxygen atoms are also expected to contribute towards the improved catalytic behavior.

Chapter 5 deals with an investigation of mono- and bi-metallic catalyst for catalytic upgradation of bio-oil to biofuel using vanillin as model compound through hydrodeoxygenation with H₂. A series of mono- and bi-metallic catalysts, namely, Ni/SiO₂, Cu/SiO₂, Ni-Cu/SiO₂, Ni-Cu/CeO₂-SiO₂, and Ni-Cu/CeO₂ were prepared by simple and facile coprecipitation method and tested under optimized reaction conditions of vanillin hydrodeoxygenation. The synthesized samples were systematically investigated by X-ray diffraction, BET surface analysis, Raman spectroscopy, high resolution transmission electron microscopy, Brunauer–Emmett–Teller surface area measurement, X-ray photoelectron spectroscopy, and H₂-temperature programmed reduction. XRD and Raman spectroscopy patterns showed the presence of cubic CeO₂ phases along with NiO and CuO phases in Cu-Ni/CeO₂-SiO₂. XPS results confirmed the presence of +3 and +4 oxidation states of Ce and +2 oxidation state of Ni and +1 and +2 oxidation states of Cu. Compared to the mono-metallic catalysts, bi-metallic catalysts showed much improved activity. Cu-Ni/CeO₂-SiO₂ (Cu:Ni=1:1) showed excellent redox property and selectivity towards hydrodeoxygenation of vanillin. The promotional effect of CeO₂ was clearly indicated by the improved activity of Cu-Ni/CeO₂-SiO₂ over Cu-Ni/SiO₂. The synergistic interaction between the Ce⁺³/Ce⁴⁺ redox couple with the Cu⁺¹/Cu⁺² redox couple, which directly participates in the catalytic hydrodeoxygenation process was held responsible for the promotional effect. The improved activity of Cu-Ni/CeO₂-SiO₂ over Cu-Ni/CeO₂ was understandable from the higher BET surface area.

The outcome of the thesis work shows the significance of CeO₂-based materials in industrial redox catalysis. Though, pristine CeO₂ has limitations of lower OSC and less structural stability at higher temperature, the investigations carried out in this thesis work successfully demonstrated favorable manipulation of reducibility of CeO₂ by use of dopants, support material, promoters, *etc.* The correlation of the catalytic activity with physicochemical properties studied in the presented work is expected to serve as an important guide in future works in this area.