DESIGN OF NANOSIZED CERIA-ZIRCONIA MIXED OXIDES FOR CATALYTIC APPLICATIONS

SYNOPSIS

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Ceria (CeO_2) containing materials are the subject of numerous investigations recently owing to their broad range of applications in various fields. Ceria is one of the most important components of fluid cracking catalysts (FCC) and three-way catalysts (TWC) [1,2]. Other significant applications of cerium oxide based catalysts include removal of soot from diesel engine exhaust, removal of organics from waste-waters, as an additive for combustion catalysts, and in fuel cell processes [1-4]. In all these applications, two unique features are responsible for making CeO_2 a promising material for use either as a support or as an active catalyst. These are (a) the Ce^{3+}/Ce^{4+} redox couple, with its ability to shift between CeO_2 and Ce_2O_3 under oxidizing and reducing conditions, respectively, and (b) the ease of formation of labile oxygen vacancies [5]. However, the oxygen storage capacity of pure ceria is unsatisfactory for practical uses. CeO_2 crystallizes in the fluorite structure in which each cerium ion is coordinated to eight oxygen neighbours, making CeO_2 more stable and reduction of Ce(IV) to Ce(III) is unfavorable. One of the best approaches to tackle this problem is substitution of another metal/metal oxide into the ceria lattice thereby facilitating the formation of composite oxides. Ceria easily forms solid solutions with other rare earth elements and with elements belonging to the transition-metal series. Replacement of cerium ions by cations of different size and/or charge modifies ionic mobility inside the lattice resulting in the formation of a defective fluorite structured solid solution. Such modifications in the structure of ceria confer new properties to the catalysts, such as better resistance to sintering and high catalytic activity [5,6].

The ability to substitute one cation for another in a particular structure is dependent on several factors, such as the dimensions of the host/guest cation and the structural features of the pure oxide. During the formation of mixed oxide phases, the structural and energetic factors of the individual constituents are profoundly modified. The resulting redox, catalytic, and thermal properties can be very different from those of pure oxides. Among the oxides of various metals such as Zr, Ca, Cu, Au, Pt, Tb, La, Mn, etc. ZrO_2 is considered to be the most interesting oxide in order to overcome the drawbacks associated with pure cerium oxide [7,8]. In the case of pure ceria, the change of Ce(IV) into Ce(III) results in a volume increase, which would restrict further change due to the increased stress energy. The presence of the smaller Zr(IV) could compensate for the volume increase. Therefore, the presence of zirconia promotes the valence change from IV to III, or III to IV in cerium ions, and consequently substantial increase in the oxygen mobility within the crystal lattice. As a consequence pure ceria is being replaced with ceria-zirconia in general. However, the unsupported $Ce_xZr_{1-x}O_2$ oxides are susceptible to a fall in the surface area due to sintering and a decrease in the stability of the structure during high temperature applications thereby loosing its oxygen buffering capacity [9,10]. In order to exploit them without loosing their unique redox features, it is very essential to synthesize nanocomposites where $Ce_xZr_{1-x}O_2$ phase is stabilized over a stable inert support.

The catalytic properties of ceria-zirconia based composites are dependent upon three main factors: particle size, chemical composition, and structural (lattice) distortion. In general, reducing the particle size of catalyst results in increasing surface area and changing its morphology, thus providing a larger number of more reactive edge sites. Especially when the particle size is decreased below 100 nm, the materials become nanophasic where the density of defects increases so that up to half (50%) of the atoms are situated in the cores of defects (grain boundaries, inter phase boundaries, dislocations etc). The high density of defects in nanophase materials provides a large number of active sites for gas-solid catalysis, while the diffusivity through the nanometer-sized interfacial boundaries promotes fast kinetics of catalyst activation and reaction. Thus, there are several advantages for switching over from conventional to nanosized materials.

Supported vanadium oxide catalysts are very complex inorganic materials that play an important role in heterogeneous catalysis in both the gas and the liquid phase reactions [11-13]. Reactions catalyzed by these oxides are numerous, including oxidative dehydrogenation of alkanes, selective catalytic reduction of NO_x with NH_3, partial oxidation of various hydrocarbons, ammoxidation of substituted aromatic compounds, and direct conversion of methane to aromatics [11-17]. In particular, oxidation catalysts are receiving a great deal of attention recently due to their major role both in the production of chemicals required by selective oxidation and in the destruction of undesired products by total oxidation. As a consequence, considerable attention has been focused on the preparation, characterization, and evaluation of vanadium oxide catalysts for various applications. Although, unsupported vanadium pentoxide is active in most of the redox reactions, its selectivity to the desired products is low and mostly favours deep oxidation. Deposition of V_2O_5 on the surface of an appropriate oxide support (mostly Al_2O_3, SiO_2, and TiO_2) of high specific surface area improves the catalytic activity and selectivity of a number of reactions. In particular, the nature of support plays a huge influence on the physicochemical and catalytic properties of the catalysts. The recent investigations reveal that V_2O_5/CeO_2 combination catalysts exhibit good catalytic activity for oxidative conversion of propane to propylene and ethylene, partial oxidation of methanol to formaldehyde, preferential oxidation of CO to CO_2 and other [18-22]. It is quite obvious since the combination of vanadia (known for its redox properties) and ceria (known for its oxygen storage and release functions) can give rise to better catalytic systems. These catalysts are also expected to perform extraneous redox reactions of both selective and non-selective oxidations, the latter having extensive applications in the field of environmental catalysis for the oxidative removal of volatile organic compounds (VOCs) and other noxious emissions.

Motivated by the unique and favourable characteristics of ceria-zirconia and vanadia based materials for various catalytic applications, a systematic and comprehensive investigation was undertaken against the above background. In this study a series of catalytically important supported ceria-zirconia [CeO_2–ZrO_2/M_xO_y; (M_xO_y = SiO_2, TiO_2, and Al_2O_3)] nano-composite oxides possessing high specific surface area, better thermal stability, good mechanical strength, superior sintering resistance, and desired redox properties have been synthesized through soft chemical routes. The obtained composite oxides were impregnated with a monolayer equivalent of vanadium pentoxide. These samples were further subjected to thermal treatments from 773 to 1073 K in order to understand the nano-structural evolution and physicochemical characteristics of these complex oxide systems. Various physicochemical characterization techniques namely, differential thermal analysis (DTA/TGA), X-ray diffraction (XRD), high resolution transmission electron microscopy (HREM), Laser Raman spectroscopy (LRS), X-ray photoelectron spectroscopy (XPS), and BET surface area (SA) methods were employed to investigate these oxide systems. The synthesized supported $Ce_xZr_{1-x}O_2$ catalysts were evaluated for the potential oxygen storage capacity (OSC) and CO oxidation to CO_2 while the vanadia-loaded counterparts were investigated for the oxidative dehydrogenation (ODH) of ethyl benzene to styrene. Thus, the thesis primarily deals with the investigation of synthesis, characterization and activity of various supported ceria-zirconia mixed oxides and the corresponding vanadium oxide loaded catalysts, aiming at the enhancement of performance and thermal (textural) stability of these multi-component catalyst systems. The thesis has been organized into six individual chapters.

A thorough literature survey on the significance of ceria in catalysis and other areas, enhanced redox properties of CeO_2–ZrO_2, and potential applicability of ceria-zirconia based catalysts are described in detail with relevant references in **Chapter 1**. Importance of supported ceria-zirconia materials formulated in the present investigation [CeO_2–ZrO_2/M_xO_y; $M_xO_y = SiO_2$, TiO_2, and Al_2O_3], significance of the corresponding supported vanadium oxide catalysts [V_2O_5/CeO_2–ZrO_2/M_xO_y] have been discussed at length in this chapter. The main objectives and scope of the present investigation are also clearly outlined.

Chapter 2 deals with the experimental procedures and the techniques employed in this investigation. The details pertaining to the preparative methodologies employed to obtain the supported ceria-zirconia mixed oxides and the corresponding vanadia impregnated catalysts are presented with appropriate references in this chapter. The experimental details related to BET SA, TGA/DTA, XRD, LRS, and XPS are given with necessary theoretical background. The method of specimen preparation and mode of operation chosen for recording the high-resolution electron microscopy (HREM) images of various samples are provided along with the details of selected area electron diffraction (SAED) measurements. The experimental aspects of the potential oxygen storage capacity measurements, CO oxidation and oxidative dehydrogenation reaction are also described in detail in this chapter.

Chapter 3 deals with the preparation and intensive characterization of CeO_2–ZrO_2/SiO_2 and V_2O_5/CeO_2–ZrO_2/SiO_2 catalysts by various spectroscopic and non-spectroscopic techniques. The CeO_2–ZrO_2/SiO_2 (1:1:2 mole ratio based on oxides) was obtained by an aqueous deposition co-precipitation method and a nominal monolayer equivalent of 10 wt.% V_2O_5 was deposited over its surface. These samples were subjected to various thermal treatments. The XRD results suggest that the CeO_2–ZrO_2/SiO_2 sample primarily consists of nanocrystalline cubic Ce–Zr oxides with slightly differing composition, such as, $Ce_{0.75}Zr_{0.25}O_2$, $Ce_{0.6}Zr_{0.4}O_2$ and $Ce_{0.5}Zr_{0.5}O_2$ in different proportions over the amorphous SiO_2 surface depending on the calcination temperature. The Raman measurements revealed the existence of cubic ceria-zirconia phase and establish the formation of oxygen vacancies, lattice defects, and displacement of oxygen ions form their normal lattice positions. The CeO_2–ZrO_2/SiO_2 support also accommodates a monomolecular layer of vanadia in a highly dispersed state over its surface. The O 1s, Si 2p, Ce 3d, and V 2p core level photoelectron peaks of CeO_2–ZrO_2/SiO_2 and V_2O_5/CeO_2–ZrO_2/SiO_2 are found to be sensitive to the calcination temperature. The XPS line shapes and the corresponding binding energies indicated that the dispersed vanadium oxide interacts selectively with the ceria portion of the CeO_2–ZrO_2/SiO_2 carrier and readily forms a $CeVO_4$ compound. The XRD and Raman techniques, in particular, provide direct evidence about the formation of $CeVO_4$. No significant changes in the oxidation states of V(V) and Si(IV) were noted. However, in the case of ceria, stabilization of Ce(III) was observed at higher calcination temperatures.

The HREM results pertaining to CeO_2–ZrO_2/SiO_2 indicated a well-dispersed Ce–Zr oxide nanocrystals (~5 nm) over the surface of amorphous SiO_2 matrix when treated at 773 K, and there was no apparent increase in the crystallite size upon subjecting to 1073 K. The exact structural features of these crystals as determined by digital diffraction analysis of the experimental images revealed that the Ce–Zr oxides are mainly in the cubic geometry and exhibit high thermal stability. All the results pertaining to CeO_2–ZrO_2/SiO_2 and V_2O_5/CeO_2–ZrO_2/SiO_2 catalysts were compiled in this chapter and published elsewhere.

The structural and redox characteristics of ceria-zirconia/titania and the corresponding vanadia loaded catalysts are presented in **Chapter 4**. The CeO_2–ZrO_2/TiO_2 (1:1:2 mole ratio based on oxides) mixed oxide was obtained by deposition co-precipitation method and a nominal monolayer equivalent of 5 wt.% V_2O_5 was deposited over its surface by a wet impregnation technique. In this case, the XRD analysis showed that depending on the treatment temperature, formation of different cubic and tetragonal Ce–Zr oxide phases, $Ce_{0.75}Zr_{0.25}O_2$, $Ce_{0.6}Zr_{0.4}O_2$, $Ce_{0.5}Zr_{0.5}O_2$, and $Ce_{0.16}Zr_{0.84}O_2$ were noted. With increase in the calcination temperature from 773 to 1073 K, the intensity of the lines pertaining to cubic $Ce_{0.6}Zr_{0.4}O_2$ and $Ce_{0.5}Zr_{0.5}O_2$ phases increased at the expense of intensity of $Ce_{0.75}Zr_{0.25}O_2$ indicating more zirconia incorporation into the ceria lattice. Impregnation of vanadia on ceria-zirconia/titania enhanced the crystallization of Ce–Zr oxides and TiO_2. However, no crystalline V_2O_5 was observed from XRD and RS measurements. In particular, a preferential formation of $CeVO_4$ compound and intense tetragonal $Ce_{0.16}Zr_{0.84}O_2$ phase were noted beyond 873 K. The XPS electron binding energies indicate that ceria, titania, and vanadia are mainly in their highest oxidation states, Ce(IV), Ti(IV), and V(V). Formation of Ce(III) has also been noticed in both CeO_2–ZrO_2/TiO_2 and V_2O_5/CeO_2–ZrO_2/TiO_2 samples at all calcination temperatures.

The HREM results show that in the case of CeO_2–ZrO_2/TiO_2, a well-dispersed Ce–Zr oxide of the size ~5 nm over the bigger crystals (~40 nm) of TiO_2 when treated at 873 K. The digital diffraction analysis of the HREM images revealed that the Ce–Zr oxides of the size ~8 nm over the surface of bigger crystals of TiO_2 are formed at 1073 K, and TiO_2 is stabilized in the anatase form. A further enhancement in the crystallite size and zirconia-rich tetragonal phase was noted in the case of vanadia loaded samples. More details pertaining to these composite oxides are elaborated in this chapter and published elsewhere.

Chapter 5 deals with structural evolution and physicochemical characteristics of CeO_2–ZrO_2/Al_2O_3 and V_2O_5/CeO_2–ZrO_2/Al_2O_3 samples. The CeO_2–ZrO_2/Al_2O_3 composite oxide (1:1:2 mole ratio based on oxides) was obtained by a deposition co-precipitation method and a 10 wt.% V_2O_5 was deposited over its surface. Despite high loading, the addition of alumina resulted into remarkable stabilization of $Ce_xZr_{1-x}O_2$ nano-crystals against thermal sintering at higher temperatures. Alumina remains as an inert carrier and does not form any unfavorable inert compounds with ceria or zirconia. The XRD analysis of samples calcined at 773 K revealed the presence of two cubic phases with the composition, $Ce_{0.6}Zr_{0.4}O_2$ and $Ce_{0.5}Zr_{0.5}O_2$. The impregnation of vanadia resulted into a stable V_2O_5/CeO_2–ZrO_2/Al_2O_3 catalyst upto 873 K. Dispersed vanadia was found to enormously affect the physicochemical characteristics of ceria-zirconia solid solutions by interacting strongly and selectively with ceria portion of the CeO_2–ZrO_2/Al_2O_3 composite oxide above 873 K. The impregnated vanadia was found to act as a driving force for the disproportionation of cubic $Ce_{0.6}Zr_{0.4}O_2$ and $Ce_{0.5}Zr_{0.5}O_2$ phases into thermodynamically more stable cubic $Ce_{0.75}Zr_{0.25}O_2$ and tetragonal $Ce_{0.16}Zr_{0.84}O_2$ phases accompanied by the emergence of a stable $CeVO_4$ phase during high temperature calcinations. The XPS measurements indicated stabilization of Ce(III) at higher calcination temperatures and no significant changes in the oxidation states of Zr(IV) and V(V). The HREM results ascertained the formation of intermixed oxides of Ce-Zr, whose grain size does not increase above 5 nm upon increasing the calcination temperature from 773 to 1073 K in the case of CeO_2–ZrO_2/Al_2O_3. However, for the vanadia-loaded samples calcined at 1073 K, the size of $CeZrO_x$ crystals ranged between 12–50 nm. More details pertaining to this interesting catalytic system are presented in this chapter.

Chapter 6 deals with the relative influence of different supports (SiO_2, TiO_2, and Al_2O_3), effect of dispersed V_2O_5 on the crystal structure and physicochemical properties of Ce-Zr solid solutions and catalytic activity studies. As revealed by XRD, in all the cases zirconia content increases gradually in the cubic fluorite type ceria lattice upon increasing calcination temperature. The CeO_2–ZrO_2/SiO_2 samples exhibit highest resistance to sintering at elevated temperatures. The impregnation of vanadia over supported CeO_2–ZrO_2 and subsequent calcination at higher temperatures leads to various modifications. The deposited V_2O_5 is in a highly dispersed state on all mixed oxides when calcined at 773 K. Particularly, the dispersed vanadia further induces better crystallization of various $Ce_xZr_{1-x}O_2$ phases and a preferential formation of $CeVO_4$. Incorporation of more zirconia into the $Ce_{0.75}Zr_{0.25}O_2$ cubic lattice leading to the manifestation of $Ce_{0.16}Zr_{0.84}O_2$ tetragonal phase at higher calcination temperatures is noted. XPS analysis in combination with XRD and Raman results was helpful to ascertain the non-formation of any undesired inert compounds between various oxide components in each composite oxide catalyst prepared, such as $Ce_{9.33}(SiO_4)_6O_2$, $ZrSiO_4$, $CeAlO_3$, $ZrTiO_4$, ZrV_2O_7 and Ce–Ti-oxides. The HREM results revealed a well-dispersed $Ce_xZr_{1-x}O_2$ nanocrystals of the size around ~5 nm over SiO_2, Al_2O_3 and TiO_2 oxides, when calcined at 773 K. The CeO_2–ZrO_2/TiO_2 sample, when treated at 1073 K, showed a small increase in size from ~5 nm to a mean value of ~8 nm for Ce–Zr oxide and no significant changes in TiO_2 anatase phase. However, in the case of CeO_2–ZrO_2/SiO_2 and CeO_2–ZrO_2/Al_2O_3, there is no apparent increase in the size of Ce–Zr-oxides. The CO oxidation activity of supported ceria-zirconia samples revealed that alumina supported samples are better than titania and silica supported samples. The potential oxygen storage capacity measurements revealed highest total OSC value for the CeO_2–ZrO_2/Al_2O_3 sample, followed by CeO_2–ZrO_2/TiO_2 and CeO_2–ZrO_2/SiO_2 indicating a strong dependence of CO oxidation activity on OSC. Interestingly, the investigation of catalytic performance of vanadia dispersed supported ceria-zirconia solid solutions towards oxidative dehydrogenation of ethylbenzene revealed stable activity during time-on-stream experiments, with high selectivity to styrene.

More details pertaining to these composite oxides are elaborated in this chapter. The detailed procedures of the synthetic process of these multi-component nano-composite oxides have been patented. As concluded at the end of the thesis, this comprehensive investigation establishes the enormous potential of the formulated CeO_2–ZrO_2 - based multi-component oxide catalysts for various catalytic applications.

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