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Catalytic aspects of ceria-zirconia solid solution: Part-I
An update in the synthesis, properties and chemical reactions of ceria zirconia solid solution

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ABSTRACT

Ceria-zirconia (CZ) solid solution is a promising ecofriendly catalyst for a wide variety of applications in the research field with unlimited role in modern technology. It is a possible alternative solution to the technology industries due to the fact that it fulfils the concept of the zero emission of automotive exhaust gas. The preparation method and composition of the components could determine the particle size, homogeneity, reliability and textural as well as the morphological properties of the CZ solid solution. The properties like surface area, pore volume, pore size, thermal and mechanical stability and surface features have been recognised as the vital parameters inducing the increased catalyst activity in CZ solid solution. This overview paid much special attention on the characteristics, synthesis methods, effect of metal dopants and supports on the CZ solid solution, along with the chemical reactions catalysed by them. Redox property, oxygen storage capacity, effect of composition, calcination temperature, chemical filing process, super-acid properties of CZ solid solutions are also discussed.

Keywords: Ceria-zirconia solid solution, Metal doping, Redox properties, Catalytic activity, Chemical reactions.

INTRODUCTION

Ceria containing materials have been under great exploration in recent years for their expediency in a number of applications in various fields of chemistry. During the last few years, ceria-zirconia (CZ) solid solution has played an important role in the heterogeneous catalysis in many applications and it fulfils the concept of the zero emission of automotive exhaust gas. According to the extraordinary achievement to applications in many areas of chemistry, a large number of studies have been concentrated on CZ solid solutions in modern centuries. Yuan et al. [1] reviewed the ceria based nanomaterials in detailed. Ceria is a promising eco-friendly redox catalyst for a large number of industrial as well as lab scale reactions, especially for automotive exhaust gas conversion, hydrogen production, water gas shift reactions etc., because of its virtuous redox property. It was used in many catalytic reactions with oxygen as a reactant based on its redox nature at lower operating temperature compared to other oxides [2]. It is well known for its redox property based on its capacity to oscillate between two oxidation states +3 and +4 [3]. The most important feature associated with the ceria is that it stores the oxygen in aerobic conditions and releases the oxygen in anaerobic conditions in order to satisfy its stoichiometry. This characteristic feature of ceria is termed as oxygen storage/release capacity (OSC) [4-6], which is responsible for all the characteristic properties of ceria. A large number of studies are investigated to understand the redox nature of ceria. However the oxygen storage capacity and thermal stability of pure ceria [7] is limited because of the lack of surface area at higher temperatures due to the nucleation and growth of crystallites of ceria within the pore [8, 9]. The inactivity of the ceria is mainly due to the non-stoichiometry in its form. However ceria can be considered as a good catalyst or support for a large variety of organic reactions and also in automobile catalysis for the intoxication of poisonous gas [10-13].

In order to overcome the limitations of pure ceria, the addition of some rare earth oxides such as lanthanum, yttrium, zirconia, silica etc. has been introduced and they improved the OSC and thermal stability of ceria by keeping its pore parameters [4, 5, 14-20]. It is well-known that the rare earth metal ion doping can upgrade the ionic conductivity of ceria and boosts its catalytic activity by providing lattice oxygen from the bulk to the surface [21, 22]. Masui et al. [23] reported that the sintering of ceria at high temperatures can be lowered by the doping of tetra or trivalent cations with ceria. The redox assets are powerfully heightened by the incorporation of external cations including Zr, Gd, Pr, Tb and Pb in to the ceria lattice by the formation of solid solutions [24-29]. The replacement of cerium cations by cations of different size and charge modifies the mobility of ions in the lattice which results in imperfect solid solution [30]. The thermal resistance and redox nature of ceria containing solid solutions with the other metal oxides like alumina, hafnium oxide and silica were also investigated by other the research teams [24, 31-35]. For the stabilisation of ceria against sintering, Cho and Mikki et al. [26, 36] reported the doping with rare earth elements such as lanthana and Ga_2O_3 respectively, but all these have been not fulfilled all the characteristics of perfect catalysis.

It is well known that the ceria contains both Ce^{4+} and Ce^{3+} ions, which are coexist in its lattice. The trivalent cerium cation has higher ionic radius of 1.14 A° compared to the tetravalent one with ionic radius 0.97 A°. As a consequence, the nearby fluorite framework of the ceria is distorted. The incorporation of tetravalent cations into the ceria lattice, the oxygen diffusivity capacity can be affected and the ion mobility inside the lattice would also be changed with the formation of some additional distortions. These distortions can be diminished by the formation of defective structured solid solutions with tetravalent cations of smaller size like Zr^{4+}, Hf^{4+}, $Pr^{4+}$and Tb^{4+} [37-41]. Then the concept with zirconia was formulated and the perception of CeO_2-ZrO_2 solid solution displayed a worthy thermal resistance and redox capacity and some predominant features.

Among the different mixed oxides with ceria, ceria-zirconia mixed oxides were caught the attention of the research field based on the indication with the formation of ceria zirconia solid solution. Putna et al. [42] suggested that the zirconia has the capacity to control the structure and sites of ceria crystallites for better performance. The incorporation of zirconia into the ceria lattice meaningfully raises the oxygen storage capacity in addition to the thermal resistance [43-46]. But there is some significant problems initiated by the formation of this mixed oxides mainly the segregation i.e. the vacancies created from the inclusion of other tetra/trivalent metal ions. These imperfections originate the modification of surface properties of the catalytic system, mainly the acid and basic sites, which are significant for its activity [38, 41].

Now ceria-zirconia solid solutions were found to have extensive applications in the TWC, as catalysts for production of hydrogen, conductors for fuel cells etc. It provides an unlimited guaranteed presentation in various high-tech fields. Some of the areas are in the field of solid oxide fuel cells, gas sensors, steam electrolysis field etc. [47]. The CZ solid solutions are now used as the stable solid state reference material in the low cost gas sensors especially in oxygen sensors because of their high OSC and thermal stability [48]. Also the ceria stabilised zirconia-alumina nano composite finds application in the medicinal field [49]. This composite can be employed as the biomaterial for orthopaedic, aesthetics, dental and joint fractures, based on their well featured properties.

The stability of three phases of zirconia i.e. cubic, monoclinic and tetragonal mainly depends on the temperature [50-52]. Tetragonal ZrO_2 commonly finds as a catalyst or catalyst support for a variety of reactions. Reports show that monoclinic zirconia is more catalytically active than tetragonal due to its special surface features and crystal structure [53]. Li et al. [54] reported the solvothermal transformation of tetragonal zirconia to pure monoclinic form. A large number of researches are investigated about the phase transformation of zirconia crystals. The phase transformation of the tetragonal to monoclinic of zirconia leads volume expansion, which causes the disastrous breakdown of the catalytic system. Hence the catalytic use of zirconia is also limited and/or restricted. To increase its applicability, use of some additives was put forwarded. Because of this drawback of zirconia alone, CZ solid solution has received so much attention of the research field.

The major catalyst activity of CeO_2 can be achieved by doping Zr ions. This is due to the high redox and high oxygen storage capacity of the developed CZ solid solution by creating physical defects and speed up the diffusion rate of the lattice oxygen present in the solid solution [55-59]. As consequences, it was wildly used in the catalysis field. Like as described earlier, the incorporation of zirconia into the ceria lattice was significantly modifies the oxygen storage capacity in addition to the thermal resistance [43-46, 60-68], based on the fact that the introduction of Zr^{4+} lowers the energy for the reduction of cerium ion and is responsible for the increased redox behaviour and OSC. It was established that the supplement of Zr^{4+} into the ceria lattice progressively distorts its cubic lattices and the higher zirconium content generates an advanced lattice distortion, therefore altering the crystalline cubic symmetry in to tetragonal symmetry [69, 70]. The high reducibility and improved OSC of the CZ solid solution is mainly due to the presence of structural imperfections which results the mobility of oxide anions at the reasonable temperatures.

Ceria–zirconia solid solution is broadly engaged as an organiser in TWC and which shows large focus of surface and bulk oxygen vacant sites, interchange of surface oxygen with gas-phase oxygen and high diffusion rates of bulk oxygen towards its surface. These features are mainly due to the presence of the redox couple of ceria [71-77]. Fu et al. [78] investigated the mechanical properties of CeO_2-ZrO_2 solid solution system in terms of fracture toughness and micro hardness. They studied that the fracture toughness would rise with grain size at the submicron scale and this feature was detected in the $Ce_{0.25}Zr_{0.75}O_2$ solid solution and suggested that a high fracture toughness that may be attributed due to the fine grain size and also due to the transformation toughening. It is well known that the acid strength of the mixed oxide may change with the charge to radius ratio of the cations. Pengpanich et al. [79] reported that the main reason for the formation of acidic sites in the CZ solid solution is due to the different charge to radius ratio of the Zr and Ce, based on the fact that ceria is more ionic than that of the zirconia and also the ionic radius of Zr^{4+} is lower (0.84A°) than that of cerium cation (0.97A°) since both of them have same metal oxygen stoichiometry. Incorporation of zirconium ions into the ceria unit cell, or vice versa, promotes the surface acid-base sites [38]. Since The Zr^{4+} ion has smaller ionic ratio than that of Ce^{4+} and can cause the generation of strong acid sites in the solid solutions. Moreover the Ce^{4+} ion destroyed the lattice structure of ZrO_2 which increased the surface area and the number of surfaced acid, and caused higher super acid activity of solid solution [41, 80-82]. Reddy et al. [83] reported the strong acidic sites in their sulphated solid solution sample. There is a key problem associated with the formation of mixed oxides, the segregation caused by the vacancies originated from the inclusion of different ions. These defects cause amendment of surface properties, such as acid and basic sites.

A large number of studies are investigated on the electrical behaviour of pure ceria either in bulk form or in the nanocrystalline form. Superior electronic conductivity has been shown by the nanocrystalline ceria in comparison with the bulk form. There are only a few reports that have been established regarding electrical conductivity of the CZ solid solution. The electrical property studies are concentrated because of its application as electrode materials for solid fuel cells, electro chromic devices, optic devices, electrical devices and also for the micro batteries [84]. Boaro et al. [85] explained the electrical properties of nanocrystalline solid solution. They found that the ionic as well as the electronic conduction may be due to the non-ideal oxygen partial pressure of the solid solution because it is depended on the conductivity. Electronic conduction is almost same for the nanocrystalline and the ceramic oxide but much better ionic conductance was observed by the nanocrystalline CZ sample due to the higher mobility of oxide anion vacancies in accordance with the entropy concept.

Previously Kaspar and Fornasiero [86] had reviewed the role of pure and alumina supported CZ system as the promoters of the automotive exhaust catalysis and Sobukawa [87] reviewed their achievements on the development of the CZ solid solution catalysis. In this review, a comprehensive discussion has been made on the recent developments in the features of CZ solid solution along with the areas such as the different methods employed for preparation and their peculiarities, effect of metal loading, the influence of supports on the CZ solid solution in various points of view and also the various chemical reactions and catalytic activity involved. Part I of the review covers most of the recent developments that have achived in the important structural and property studies of ceria zirconia solid solution. Part II will be more specific, which focus on the progressive heterogeneous catalytic applications of metal doped CZ solid solution in recent years especially in TWC, hydrogen production methods, in soot oxidation and also in its achivements in the developments of oxygen gas sensors.

2. Properties of CZ solid solution

2.1. *Redox property*

One of the most important characteristicproperties of CZ solid solution is its redox nature. CZ solid solution shows good redox properties [88, 89] than that of zirconia, mainly due to the result of a large number of defect sites on the surface and the capacity to produce high rate of oxygen vacancies [90]. Geometrical structure of solid solution is the responsible factor for the redox properties including the oxygen storage capacity [91]. Aneggi et al. [92] studied more clearly the redox properties of the CZ solid solutions. They explained reduction properties based on the temperature programmed reduction (TPR) studies. Since ceria losses its characteristic property such as OSC at high temperatures, also the redox properties are diminished.Hence it can be say that the CZ solid solution has better redox property than that of ceria at high temperatures. The introduction of the non-reducible zirconium ion into the ceria lattice may cause the increased redox property of ceria by the enhancement of its oxygen storage capacity [93]. The presence of Zr reduces the reduction temp of Ce^{4+} to lower temperature and also increases the total amount of the reduced cerium. They suggested that the surface area is weakly dependent on the extent of reduction and even though reduction capacity was observed for the all range of CZ compositions, intermediate compositions showed the large reduction capacity.

Reduction of ceria proceeds through Ce^{4+} surface reduction and the Ce^{4+} bulk reduction at higher temperatures. In the TPR diagram of ceria, two peaks are seen due to the involvement of both small and large crystals of ceria in the reduction process at high temperature. But in the case of CZ solid solution, there is only one peak is shown by the TPR result indicates that the reduction features of all crystals in solid solution are same [92]. The reduction process of CZ solid solution normally comprises two steps, first one is the reduction at the surface generating oxygen vacancies and the second is the migration of oxygen vacancies into the bulk. Fornasiero et al. [94] investigated the redox properties of rhodium loaded ceria rich CZ solid solution with rhodium nitrate and chloride precursors. They investigated that hydrogen activation is expressively large in the system prepared from nitrate precursor in comparison with the chloride precursor. Along with this, they postulated that the development of oxygen vacancies is more general for nitrate precursor and the same is also depended by the system prepared from the chloride precursor. They concluded that chloride centred synthesis, have a harmful outcome on the OSC of the CZ solid solutions, in the TWC aspect. Gennari et al. [95] studied that the addition of a bit quantity of chloride ion to the surface of the CZ solid solution can enhanced oxide ion vacancy development and the scrambling process,which are the factors for redox behaviour.

2.2. *Oxygen storage capacity (OSC)*

OSC is the key parameter of TWC which is related to the operating conditions and is defined as the quantity of oxygen stored or released by the catalysts and can be utilised for the oxidative reactions. Commonly, there are two types of OSC, total and dynamic OSC. Total OSC denotes the quantity of oxygen thermodynamically accessible and the quantity of kinetically available oxygen are termed as the dynamic OSC, both of these has been studied by using the thermal analyses like temperature programmed reduction or oxidation, thermo gravimetric etc. [96-98]. Mainly three methods were used for the determination of OSC. They are (1) temperature-programmed reduction or oxidation using some probe agents like CO and H_2 [97, 98]. (2) Pulse experiments with time persistence [99] and finally (3) Oxygen chemisorption at room temperature [100] followed by the chemisorption of hydrogen for measuring the available number of oxygen species present in the sample for the redox reactions and hence the OSC of solid solution sample is resulted. The amount of chemisorbed oxygen will give the OSC of the material.

Sakamoto et al. [97] reported the OSC measurement of CZ solid solution on the millisecond scale using two CO pulses with millisecond pulse width. They suggested that the rate of release of oxygen is the important feature of catalysts in addition to the total OSC. Aneggi et al. [92] reported that in the cubic fluorite type structure of ceria, one Ce ion is surrounded by 8 oxygen atoms at the corners of a cube. By the zirconium incorporation, the replacement of cerium ion, by Zr^{4+} ion takes place because the ionic radii of Zr^{4+} is very small in comparison with the ionic radius of Ce^{4+} ion generating defects in the lattice of CZ solid solution and that causes the alteration of surrounded oxygen. The distortion of oxygen will develop the OSC of solid solution and the distortion of oxygen increases with the Zr content and this is the main factor responsible for the symmetry transition of solid solution from cubic to tetragonal. Larrondo et al. [101] reported the nickel loaded CZ solid solution for the partial oxidation of methane and found the absence of any carbonaceous deposits on the catalyst, with high catalyst stability, which is mainly due to the high oxygen storage capacity of ceria rich CZ solid solution. Thus clear that OSC is responsible for the non-deposition of carbon/coke on the sample. Fornasiero et al. [102] investigated that the incorporation of zirconia into the Rh/ceria will promote the bulk reduction behaviour of the system and which is responsible for the large OSC of the system, due to the formation of a CZ solid solution. Main explanation for the OSC is provided by the Nagai et al. [103]. They investigated that during the oxygen releasing process, the oxidation state of cerium changes between +4 to +3. At that time there is a volume expansion takes place resulting the formation of some stress energy, which further prevents the oxidation state change from +4 to+3. The volume expansion is compensated by the zirconium incorporation and the valence change can be promoted. Thus it is clear that the improvement of the homogeneity of the components in the CZ solid solution promotes the OSC.

Yang et al. [104] reported that the introduction of Zr ions makes some imperfections on ceria and results in the formation of oxygen vaccanciesresulting OSC. They reported that these oxygen vacancies can help smaller Zr^{4+} ions to provide some extra space for accepting the cerium ions. Dutta et al. [105] reported that the development of OSC in the solid solution mainly due to the presence of alarge number of strongly and weakly destined oxygen in the solid solution and which is absent in the pure ceria. Wang et al. [96] reported that the CZ solid solution have better dynamic OSC due to the higher migration rate of the lattice oxygen compared to the pure ceria. Bedrane et al. [106] prepared the noble metals like Rh, Pt, Pd, Ru and Ir loaded CZ solid solutions and investigated their OSC. They established that the OSC was improved by the existence of noble metals on the CZ solid solution. But iridium and ruthenium showed best OSC among the other noble metals. The metal particles act as “portholes” for the successive storage and release of oxygen in the CZ solid solution and noted the general trend of increase that is investigated by previous reports.

Luo et al. [107] discussed the increased OSC of ceria and CZ oxides alone and also under SO_2 environment and reported that at lower temperatures, ceria reacts with $SO_2$and forms the sulphite species whereas at higher temperatures, cerium sulphates are formed under the oxidising conditions. The sulphates are then effortlessly changed to Ce_2O_2S and reversibly oxidized back to the sulphate. This phenomenon is responsible for the increased OSC under these conditions. Later it was discovered that the zirconia have a great effect in the interaction of sulphur with the ceria. Bazin et al. [108] studied the CZ oxide in the SO_2 environment and suggested that the sulphates on the ceria-zirconia mixed oxide were more easily reduced than sulphates on pure ceria and a high OSC is observed in the CZ system. Nelson et al. [109] reported the effect of SO_2 introduction on the ceria-zirconia mixed oxides and postulated the improved sulphur tolerance. Liu et al. [110] reported that the stability of sulphate assemblies on ceria rises upon development of solid solutions with zirconia. Luo and Gorte [111] also investigated that at 200°C bulk sulphates are formed on ceria and only surface sulphates are formed on ZrO_2. For the CZ solid solution the amount of sulphates formed at 400°C improved linearly with the ceria content.

Dong et al. [112] reported Pt loaded CZ solid solution with best OSC capacity. They investigated that the OSC capacity may be due to the well dispersion of Pt on the CZ surface, specific surface area of ceria-zirconia and also due to the homogeneous dispersion of zirconia in ceria. Kondratenko et al. [113] studied the CO oxidation in the absence of oxygen over the Pt loaded CZ systems for the measurement of the OSC. They described the OSC as the ratio of the amount of CO_2 produced to the total amount of Ce atoms, which depend on the extent of dispersion of Pt particles and the homogeneous delivery of zirconia on the ceria lattice and demonstrated that the OSC is ruled by the Pt particle with large surface area and the well zirconia distribution on the ceria lattice. Ghom et al. [114] investigated the mesoporous CZ solid solution prepared through the hard template method and reported that the system showed high OSC compared to the mesoporous ceria, due to the presence of replacement of zirconium in the ceria lattice even at low zirconium percentages (5%). Nagai et al. [115] claimed that the OSC of the CZ system will be improved by increasing the homogeneity of Ce and Zr atoms in the solid solution. Nagai et al. [103] described the relationship between high OSC and the atomic structure of the solid solution. Their group prepared the solid solution in 1:1 molar ratio and established that the main factor for the improved the oxygen storage capacity is the homogeneity of cerium and zirconium atoms in the solid solution. The explained mechanism was that the introduction of zirconium ions in the ceria may cause the ease of valence change or the oxidation state change from +4 to +3 in ceria along with the result of shortening the Ce-O bond length in solid solution. As a result of this, the configurations of oxygen atoms around the Zr ion will become more centro-symmetric co-ordination. These two changes in the oxygen environment around the Ce and Zr ions will facilitate the generation of active oxygen, which are responsible for the high oxygen storage capacity of the solid solution.

3. Effect of various parameters on the properties of CZ solid solution

3.1. *Effect of composition*

Composition has an extraordinary effect in the nature and properties of CZ solid solution. Pure ceria-zirconia solid solution exists in different phases mainly as cubic and as tetragonal in accordance with the cerium content present in the sample. If the molar content of ceria in the solution is lower or equal to 50 %, then it can be tetragonal, otherwise it appears as cubic same as that of ceria. Zhang et al. [116] demonstrated that Ce/Zr ratio have a great influence on the phase composition. It is concluded that the ceria rich solid solution compositions have cubic and zirconia rich compositions have tetragonal phase respectively. At the moderate composition of ceria and zirconia, both phases are detected and reported the existence of a cubic-tetragonal phase, which can enable catalytic activity in the reaction.Enzo et al. [117] reported the same that the ceria rich compositions have cubic and zirconia rich composition have the tetragonal phases respectively. Aneggi et al. [118] reported that among the various compositions of solid solution, the equilibrium composition is the most promising one because of its prime redox properties associated with its stabilised phase. Kaspar and Fornasiero [86] investigated that the phase composition of the CZ solid solution plays an important role in the three way catalytic applications. It is established that the solid solution containing a single-phase is superior for the three way catalytic applications, related to the phase segregated CZ mixed systems. Also it is well known that the Ce/Zr ratio in the CZ solid solution plays a major role in the response of the special features mainly the thermal stability and the oxygen storage capacity. It should be common that the increased amounts of zirconium in the solid solution may increases the total acidity of the catalyst, which is higher than that of zirconia whereas the more redox property is shown by samples with more cerium content, based on its oxygen storage capacity. Higher zirconium content can reduce the surface area. The introduction of zirconia in the cubic ceria lattice may cause the generation of a defect in the mixed oxide which promotes the mobility of lattice oxygen and the redox reaction takes place at the surface as well as at the interior of the solid solution [119-121]. With increase in the cerium content in the solid solution, the segregation of phases in the CZ system will be increased. Aneggi et al. [92] reported that it is impossible to find a composition at which phase separation of solid solution occurs, because this feature depends on the method preparation and the heat treatment [38, 41]. Many results show that ceria-rich composition prefers a cubic symmetry while neutral and zirconia-rich compositions crystallises with a tetragonal phase. An optimum ratio of the defects and Ce content is needed for the high activity of ceria-zirconia solid solutions [81, 83].

The high OSC of CZ solid solution is mainly due to the formation a homogeneous solid solution [122]. Most acidic catalyst with large zirconia content showed the higher activity which is mainly due to the easy availability of lattice oxygen in the system [123]. Sohn et al. [124] reported that the cerium content may promote the activity of sulphated zirconia by providing a solid solution with thermal resistance and large surface area, also providing the strong acid sites for the acidic reactions [125,126]. Guo et al. [127] investigated that the surface area of CZ solid solution improved with increasing of Ce/Zr ratio, whereas the thermal resistance is reduced in accordance with the Ce/Zr ratio. Katta et al. [128] prepared the pure ceria, ceria-zirconia (CZ) and ceria-lanthana (CL) for comparison of effect of composition by the co-precipitation method for the low temperature soot oxidation reaction. The presence of oxygen vacancies and lattice defects are detected in both the CZ and CL samples but more prominent in the CL catalyst due to the large concentration of redox couple in the CL compared to the solid solution. They investigated that La^{3+} doped ceria speed up the oxidation rate of soot compared to pure ceria and the solid solution may be due to the better active oxygen formation rather than the solid solution. Related to CZ, the CL sample presented a much high OSC, high thermal stability and improved soot oxidation activity. CZ solid solutions with high Ce/Zr surface ratio values have no phase segregation while lower values indicate the phase segregation.Damyanova et al. [129] reported that the zirconia preserves its tetragonal structure in all CZ solid solution compositions based on the fact that they contain a huge number of defects in their sites due to the strong interaction with the ceria species. If the ceria content is very high, then a fluorite cubic ceria structure is observed on surface of the zirconia. The solid solution provides better redox characteristics than zirconia due to the huge number of defects and has the power to create the oxygen vacancies. Kenevey et al. [130] reported the effect of composition in CZ solid solutions. They studied that, for the $Ce_{0:50}Zr_{0:50}O_2$ solid solutions, the tetragonal phase undergoes demixing during calcination, resulting the formation of a ceria rich and zirconia rich compositions. Throughout the progress of the calcination, these compositions preserves and no intermediate compositions are formed and also noticed that for other systems (ceria and zirconia rich compositions) this type of behaviour is not observed.

Galtayries et al. [131] investigated that addition of ZrO_2 in to the solid solution further advances the redox property and hence also the catalytic activity of the solid solution. Bozo et al. [132] investigated the role of CZ solid solution in comparison with the alumina in various metal loaded forms. It is a clear evidence for the greater activity of the solid solution. Fornasiero et al. [102] investigated that the incorporation of zirconia into the Rh/ceria promoted the bulk reduction behaviour of the system and which is responsible for the large OSC of the system. Also suggested that the OSC is greatly predominated in the case of cubic one compared to the monoclinic and tetragonal phase. Yashima et al. [133] investigated that, for the binary system of CZ solid solutions, there are three possible structures: monoclinic, tetragonal, and cubic; and several stable or metastable phases having tetragonal symmetry were established. Wang et al. [134] reported that the phase composition of the CZ solid solution be determined by the percentage of ceria present in it, which corresponds to the grade of reducibility power both in the bulk and also in the surface.They also investigated that the pure zirconia and the CZ solid solution containing 1wt% ceria have the tetragonal and monoclinic phases respectively. But the solid solutions containing 25 and 50 wt. % ceria provided the cubic structure.Table 1 illustrates the phase composition more clearly.

Table 1. Illustration of the phase composition

Summary of CZ solid solution ($Ce_xZr_{1-x}O_2$) composition			
x value	Phase	Description	Reference
< 0.15	Cubic fluorite	-	[135, 136]
> 0.85	Monoclinic	-	[136, 137]
Intermediate compositions	Different tetragonal phases and the meta- stable cubic phase (kappa)	Metastable cubic phase, termed as kappa, which has an ordered organization of cations with a pyrochlore type structure	[137, 138]

Crespo et al. [139] reported that due to the phase separation process, a large range of compositions especially the intermediate compositions of solid solutions are found to be thermodynamically metastable. They also reported that the equilibrated CZ solid solution models containing more Zr content are estimated to show heterogeneity on the atomic scale and also the segregation of Zr ions in the solid solution with Ce enrichment of the surface, due to the more covalent character of Zr-O bonds related to Ce-O bonds. Yao et al. [140] invented the high surface area CZ-alumina catalyst for the composition effect study. They postulated that the alumina support exploited the interaction of Zr and Ce in the solid solution using the aid of impregnation method with cubic symmetry in fresh samples which is due to the high dispersion of zirconia over the alumina support (low zirconiacontent) and tetragonal symmetry in the zirconia rich samples. They also suggested the absence of cerium aluminate in the sample which is mainly due to the presence of well dispersed zirconia on the alumina support. Vlaic et al. [141] reported the well dispersed Rh containing CZ solid solution and stated that the Rh particles are effortlessly oxidised to the oxide form in presence of automotive gases even though the retaining of high dispersion at high reduction temperatures and indicated that the presence CZ support helps well dispersion of rhodium metal particles in comparison with the alumina support. The applications of CZ solid solutions are directly linked to the nature of composition especially nature of the rich component in the system.

Trovarelli et al. [142,143] investigated zirconia-rich compositions, which found application in the ceramic industry and also employed as ionic conductors in the electrical field. But ceria-rich compositions are widely used in the catalysis field. Fornasiero et al. and Trovarelli et al. [71,144] reported that ceria rich compositions have high OSC and reduction capacity compared to the zirconia rich compositions. Studies revealed that the phase diagram of CZ solid solution proved the existence of a monoclinic structure with the ceria content lies below 20% and for higher compositions from 75 to 100%, a cubic phase was reported. For the intermediate composition, due to the presence of a large number of stable and metastable tetragonal phases, the phase diagram is still not understood well. Yashima et al. [145,133] reported the co-existence of three tetragonal phases based on the Raman and XRD analysis. According to them, one of the stable tetragonal phase formed by the diffusional phase decomposition. The second metastable tetragonal phase was formed by the diffusion less transition and the last one is stated as a cubic phase as previously reported by Masui et al. [23]. Ghom et al. [114] investigated the formation of CZ solid solutions with cubic phase up to 20% of zirconium and after that, up to 50%, the formation of tetragonal phase was detected. Fornasiero et al. [71] found that the migration of oxygen is more predominant in the zirconia rich CZ solid solution in comparison with the cubic ceria rich system. The same result was obtained by the studies of Sugiura [146], also investigated that the zirconia rich compositions provide more OSC compared to the ceria rich composition. Rossignol et al. [147,148] suggested that the zirconia rich CZ solid solutions are found to be the best systems in terms of their enhanced thermal stability, acidity and the oxygen storage capacity. Watanabe et al. [149] reported that that catalytic activity of the Ni–Fe/CZ catalyst was found to be greater in comparison with the commercially available Fe–Cr-based catalyst. This is mainly due to the formation of the stabilized ordered structure of Ni–Fe/ CZ catalyst in comparison with the one without zirconia. Sohn et al. [124] reported the surface area of sulphated super acid solid solution correlated with the composition along with calcination temperature. They observed that the surface area of catalysts calcined at high temperature (650–700^{o}C) are high in comparison with the calcination at 400–600^{o}C. The high surface area of catalyst is attributed the effect of ceria in the sample for the tetragonal phase of zirconia.

3.2. *Effect of calcination temperature*

Calcination temperature plays an important role in the properties of CZ solid solution. Many studies reported that the CZ solid solution loses its surface area during calcination at high temperatures, valid explanation for this behaviour was provided by Kaspar et al. [150]. They invented that the presence of heterogeneity in the CZ solid solution will promote the phase segregation at the time of calcination, which is the main factor responsible for the lowering the surface area. Atribak et al. [151] prepared ceria, zirconia, and CZ solid solution by solid state mixing method and calcined at 1000°C. CZ mixed oxide is more active catalyst than pure ceria and zirconia calcined at the same temperature, both in loose and tight contact between soot and catalyst for the soot oxidation reaction. The main reason for that, at 1000^{o}C, the ceria loses its catalytic property due to sintering and low OSC because of low surface area and high crystal size due to the growth of crystallites. Besides this, solid solution shows high surface area and small crystal size and better redox properties, which is responsible for the better activity of solid solution. But the zirconium molar content doesn’t affect the catalytic activity. The catalytic activity of pure zirconia is found to be lower than solid solution in tight and loose contact. However in loose contact, Zr activity is almost same as that of ceria, but in tight contact of catalyst and soot, Zr shows a lower activity than ceria. The higher activity is due to the presence of bare oxides in the solid solution system even after the calcination. Sohn et al. [124] reported the surface areas of sulphated super acid solution connected with calcination temperature. They were investigated that the surface areas of catalysts calcined at high temp 650–700°C are high in comparison with the low temperature calcination (400–600°C). The high surface area of $Ce\text{-}ZrO_2/SO_4^{2-}$ is the effect of ceria in the sample for the tetragonal phase of zirconia. Chen et al. [152] investigated that the calcination temperature have a capacity to tune the structural distortion and hence the structural micro strain in the surfactant assisted CZ solid solution. They reported that the crystal microstrain increased from 2.1% at 80°C to 3.45% at 200°C degree and then to a maximum 6.72% at 400°C; later, it dropped to 4.51% at 600°C and 4.05% at 800°C. The provided explanation is that with increase in temperature, the surfactant was slowly quit from the solid solution and a higher crystal strain is resulted. At high temp there exists a strong vibration in Metal -Oxygen bond and a lower strain is noticed. Atribak et al. [153] indicated that the development of an exact solid solution avoids surface separation of Zr even though they are subjected to calcination at high temperature. They provided an explanation for the decreased NO oxidation capacity of CZ solid solution calcined at 800°C with respect to 500°C, as the decreased Ce/Zr surface ratio, which is mainly due to the surface segregation of Zr due to the calcination.

3.3. *Chemical filing process*

Chemical filing process is an effective method for the modification of redox property of CZ solid solution at lower temperatures. The main aim of chemical filing in the CZ solid solution is the enhancement of the surface active sites in the catalyst system. The high temperature reaction between CZ mixed solid solution and chloride ions constitute the chemical filing, which drops the reduction temperature of solid solution to a lower range [154,155]. Boghosian and Papatheodorou [156] stated that the excess chemical filing may be causes the phase separation in the CZ solid solution.Masui et al. and Nakano et al. [155,157] reported the chemical filing on the CZ solid solution. According to Masui et al. [155], by the surface dealing of the solid solution, the redox temperature of the solid solution is upgraded. The reduction temperatures of the chemically filed solid solutions became lower than those of the pure solid solution. They reported the surface treatment using the ammonium chloride as the chlorinating agent on the solid solution. Using the procedure, the oxygen release capacity of the solid solution was observed at lower temperatures. Nakano et al. [157] reported the use of alkali metal chlorides as the chlorinating agent for the surface treatment. It eliminated the limitations of ammonium chloride in the further poisonous gas emissions. The chemical filing process caused the formation a metastable tetragonal phase and has a good capacity to store and release oxygen. Gruen et al., Oye et al. and Boghosian and Papatheodorou [156, 158, 159] investigated that the metal chlorides will give the vapour phase complexes with the $AlCl_3$. The modification of the surface properties of the CZ solid solution with the vapour phase complexes are also termed as the chemical filing process. Masui et al. [23] investigated the process using aluminium chloride, and reported that that there are many steps in the chemical filing process, firstly the surface chlorination of CZ solid solution takes place. The extent of chlorination can be controlled by adjusting the concentration of chlorine gas and the time required for the chlorination. The chlorides of ceria and zirconia formed on the surface of the solid solution are then eliminated through the formation of gaseous complexes with the aluminium chloride. Finally on evaporation chemically filed CZ solid solutions are formed [154]. Masui et al. also demonstrated that the reduction activities of the chemically filed sample have high thermal stability and high temperature redox performance. The chemically filed CZ sample proved their high reduction behaviour at lower temperatures and get simply oxidised at 400^oC and reported that the chemical filing process leads to the upgrading of the surface area of the sample [156, 23]. All these characteristics after filing is due to the formation of active surface sites and also due to the segregation of ultrafine ceria along with the phase stability attained trough the chemical filing process. Masui et al. [154] prepared the CZ solid solution by the thermal decomposition of cerium-zirconyl oxalate and it is chemically filed with the aluminium chloride.The active surface sites of CZ are obtained by the elimination volatile complexes of aluminium chloride and chlorides of cerium and zirconium. They also investigated that the chemically filed solid solution provided better redox behaviour at lower temperatures than the CZ prepared by normal route.

3.4. *Acidity - Solid super acid catalysts*

Common acid-based liquid super acids are found be catalytically more active. But due the separation or regeneration of the spent catalyst, it is not suitable for the industrial scale applications. In catalysis field, a heterogeneous catalyst is more applicable in the sense of easy handling and separation. Therefore a large number of solid super acids are developed for the catalysis. Among them sulphated zirconia have much more attention because of its high thermal stability, high super acidic ability and higher catalytic application with lower surface area. For improving the surface area, large preparation methods are done by the researchers. The developed solid super acids are found to be catalysing the organic reactions like esterification, cracking, alkylation, and isomerization [160,161]. Sohn et al. [124] established the enhancing effect of CeO_2 on catalytic activity of sulphated zirconia and concluded that appropriate amounts of $Ce(SO_4)_2$may stabilize the surface sulphur species with the promotion of acidity of the catalyst. The catalyst showed better surface area in comparison with sulphated zirconia. On ceria doping, the solid solution acquired a stable tetragonal phase. $CeZrO_2/SO_4^{2-}$ provided good catalytic activity for the two organic reactions. 2-propanol dehydration and cumene dealkylation. Acidity of the prepared catalysts is the factor for better reactions. Guodong et al. [82] prepared the solid super acid catalyst $S_2O_8^{2-}$/ CZ via co-precipitation method and found that the incorporation of Ce into the catalyst was useful for the formation tetragonal zirconia and restricted the generation of monoclinic zirconia, and prevented the loss of sulphated species, the sample. The catalytic activities of the solid super acid were tested for the esterification of lactic acid with n-butanol. The esterification efficiency of lactic acid was about 96.6%. Hu et al. and Reddy et al. [162,163] also prepared the solid super acid catalyst through the co-precipitation method. The increased surface area of $S_2O_8^{2-}/ ZrO_2\text{-}CeO_2$ in comparison with the $S_2O_8^{2-}/ZrO_2$resulted by the introduction of the zirconium into the ceria lattice is responsible for their redox and acidic sites [83]. Acidic ceria–zirconia solid solution has been made by addition of sulphuric acid to a mixture of cerium and zirconium hydroxide precursors before subjecting to calcination and these sulphated catalysts have shown remarkable effects for the acid catalysis [164]. Reddy et al. [165] used sulphated CZ super acid solid solution for the synthesis of coumarin under solvent free conditions through the pechmann condensation reaction of phenols with methyl or ethyl aceto acetate. All the tested reactions will provided more than 80% yield with good selectivity. Azambre et al. [166] prepared the sulphated ceria–zirconia solid solutions by treating crystallized solid solution with sulphuric acid, which is found to be more acidic than the CZ solid solution.

4. Preparation methods

A satisfactory preparation method is a vital parameter in catalysis field for the development of materials. The formation of CZ mixed oxides mainly depends on the atomic ratio of Ce and Zr. It further depends on the preparation method and results in the segregation of solid solution. It also impacts the development of acid and basic properties and also the OSC.

Co-precipitation method is the most common method, employed for the preparation of CZ solid solution. Hori et al. [167] studied the influence of cerium precursor in the nature of solid solution in the co-precipitation method. For that, ammonium cerium nitrate and pure cerium nitrate salts were used as the precursors of ceria and zirconyl oxy nitrate as the Zr precursor. They concluded that the use of $Ce(NO_3)_3.6H_2O$ leads to the formation of mixed oxide with cubic ceria and tetragonal zirconia, but a solid solution is obtained by using the ammonium precursor of ceria, $(NH_4)_2Ce(NO_3)_6$. Also it is clear that cerium precursor is the most significant factor of the preparation method, since it is responsible for the crystalline phases and the redox behaviour of solid solution. Letichevsky et al. [168] also reported the same effect of ceria precursor. They demonstrated that the usage of $Ce(NO_3)_3$ as precursor directed to the development of separated ceria and zirconia phases but a solidsolution was obtained by using $(NH_4)_2Ce(NO_3)_6$ in the co-precipitation method. Hurtado et al. [169] investigated the same behaviour as the cerium precursor, either $Ce(NO_3)_3 \cdot 6H_2O$ or $(NH_4)_2Ce(NO_3)_6$, affects features of ceria-zirconia mixed oxides prepared by co-precipitation. They investigated that the precursor $Ce(NO_3)_3 \cdot 6H_2O$ (with Ce^{3+}) leads to a CZ mixed oxides with cubic fluorite structure with Ce-enrichment on the surface and an heterogeneous distribution of cerium and zirconium is observed, but a CZ solid solution with tetragonal structure was attained by using $(NH_4)_2Ce(NO_3)_6$ (with Ce^{4+}).

Fan et al. [170] reported the preparation of pure and strontium loaded solid solution by the oxidative precipitation method. Here in addition to precipitating agent, oxidising agents (H_2O_2) were added. Tadokoro and Muccillo [171] investigated the ultrafine tetragonal zirconia-ceria powders prepared through the co-precipitation technique. The usage of azeotropic distillation with the butanol promoted the physical properties of the as-synthesised CZ solid solution. The prepared systems were found to possess large specific surface area withvery small pore size of 9nm. Changlin et al. [172] reported the homogeneously disordered mesoporous CZ solid solutions with the pore size of approximate 4 nm, prepared through the co-precipitation combined with evaporation-induced self-assembly process using different templates. The catalysts obtained through this method were found to be exhibit high thermal resistance and investigated that the mesoporous nature is much less affected by the different surfactants.

Homogeneous co-precipitation method is the other employed method for the solid solution preparation. Samples obtained through this method are found to have well defined particle size with high surface area. In this method, the ceria and zirconia precursors are made in a quantitative solution with a particular molar ratio. To this solution a homogeneous precipitant like urea [173, 174] was added for the hydrolytic decompositionand to yield the precipitaiting anions. The produced anion is responsible for the precipitation of the components. Heat treatment of the stirring homogeneous solution will display a suspension, which on aging will provide a solid residue. This on further calcination yields the solid solution. Pengpanich et al. [175] synthesized nanostructured CZ oxides through the homogeneous co-precipitation method with urea hydrolysis using $Ce(NO_3)_3$ as starting material, and investigated that the formed system were not homogeneous but really segregated. Rivas et al. [176] used this method for the preparation of CZ solid solution.

Microwave assisted preparations are also done for the synthesis of CZ solid solution. Potdar et al. [177] reported the synthesis of solid solution based on the microwave hydrothermal method by applying high pressure and obtained a highly homogeneous cubic CZ solid solution. Reddy et al. [178] prepared the CZ solid solution by the carbon black copolymer surfactant assisted microwave route, and the prepared samples were found to be nanosize, mesoporous in nature and catalytically active for CO oxidation. Chenet al. [179] reported the synthesis of CZ solid solution by microwave assisted solution phase heating.In this method the precursors along with the organic surfactants are dissolved in distilled water to obtain a desired molar ratio. The formed precipitate is allowed to cool in room temperature and finally calcined to obtain the solid solution. Again Reddy et al. [180] performed the synthesis of solid solution by rapid microwave assisted solution combustion synthesis method using the dielectric heating. Important applications of this method were found to be the low energy utilisation and also the short duration of time with rapid crystallisation, also allows the preparation of binary oxide nanoparticles. Fu et al. [78,181] prepared the CZ solid solution by microwave-induced combustion by using urea as fuel. They suggested the method in which the metal nitrates and urea in water, are mixed and subjected to combustion in a microwave oven to obtain the CZ solid solution. The following advantages associated with this method as need of low time with simple processing, apparatus, and normal precursors. Clark et al. [182] studied that the microwave handling of things is basically dissimilar from old-heat treatment with respect to the method of heating. In a microwave oven, the heat is produced inside the sample itself by the collaboration of microwaves and solid. Reddy et al.[183] reported the microwave assisted synthesis of nanocrystalline CZ solid solution using urea as the fuel. The solid solutions were found to be have a homogeneously single phase with analogous specific surface area, OSC and crystallite size compared to that of the co-precipitated samples.

Another most important method is the impregnation method, in which, one of the precursors is first calcined to obtain its oxide and the other inorganic precursor is dissolved in a solvent (usually water or ethanol) according to the molar ratio and the desired temperature is selected for the addition of the prepared oxide to the solution. Then the components are stirred well and the solvent is evaporated at low temp to yield the samples, which on further calcination yield the CZ solid solution. It is found that the catalysts prepared by this route showed high surface area and virtuous thermal stability because of the strong interaction between the two oxides in the solid solution [90,184]. One of the other efficient methods for the CZ solid solution preparation is the hydrothermal method. In this method the solution of inorganic metal precursors of ceria and zirconia are vigorously mixed with aqueous ammonia solution by the maintenance of pH usually alkaline (9.5), and the slurry was then kept in an autoclave for a particular time for the hydrothermal treatment. The obtained precipitate was then purified before subjecting to calcination. Even though the method generates solid solution, the main disadvantage of this method is that the products are highly dense without surface area for its application in catalytic areas [90]. Zhao et al., Zhu et al. and Cabanas et al. [174, 185, 186] prepared the solid solution by hydro thermal method. Ceria–zirconia mixed oxides were prepared by the hydrothermal method in supercritical water, with the generation of crystallized nanoparticles by Kim et al. [187]. Zhang et al. [188] reported the surfactant assisted hydrothermal method for the preparation of gold loaded yttria containing CZ solid solution. Preetam Singh and Hegde [199] prepared the nanocrystalline CZ catalyst with the size of approximately 5-12 nm by hydrothermal method using diethylene-triamine and melamine as complexing agents. Si et al. [200] investigated the urea hydrolysis-based hydrothermal method for the preparation of the nanostructured CZ solid solutions with high homogeneity and thermal resistance.

Surfactant assisted synthesis of mesoporous materials has a strong attention based on the development of high surface area catalysts. In surfactant assisted method, aqueous solution of an ionic surfactant is homogenised with a quantitative solution of ceria and zirconia precursors in a desired molar ratio. Then the cerium and zirconium hydroxides are precipitated by ammonia solution. It is then kept in a thermostat for long time. Then the residual solid on washing, drying and on calcination yields CZ-solid solution. One of the commonly used cationic surfactant is cetyltrimethylammonium bromide (CTAB) [191]. The efficient introduction of the organic surfactants into the hydrous oxide of solid solution is adequate for the textural properties like surface area of the solid solution. Terribile et al. [191] also reported that high pH range is essential for the preparation high surface area solid solution. At lower pH, the extent of surfactant incorporation will be lower and hence a lower surface area and reported that degree of incorporation of the surfactant and the homogeneity of solid solutions was also reaction time depended. If lower time is given for the exchange of hydroxy groups of the hydrous oxide and the surfactant, then the surface area should be very lower. Laosiripojana and Assabumrungrat [192] reported this type of procedure. But there are other methods which used surfactants in their preparation. Chen et al. [152] reported that the nanophase of mesoporous ceria–zirconia solid solution with a large number of cationic defects in the crystalline structure was obtained through this method. The surfactant take part a major role in the controlling of the pore factors for their distribution and created defects in the lattice of the solid solution. The CZ solid solution showed a distortion in the structure and resulted in the development of a crystal micro strain. Fig. 1 shows the effect of surfactant, citric acid in the homogeneous agglomeration of solid solution nanoparticles prepared by the solid state mixing of precursors.

Sol gel method is another common method for CZ solid solution synthesis. In this method the component precursors are dissolved in water and then added complexing agents and dispersants (if necessary), then stirred well to obtain a sol. After that the sol is dried to gel and finally powder, which on calcination yield solid solution. Samples prepared through this method may have good structural as well as textural (like high surface area) properties [193]. Thammachart et al. [194] reported that highly uniform nanosize CZ solid solution was obtained through this method. In pseudo sol gel method, the inorganic metal precursors of ceria and zirconia dissolved in an organic precipitating agent under hot and stirring conditions. On evaporation the contents may provide a gel, which on normal treatment results in the CZ solid solution. Vargas et al. [195] synthesised the cubic fluorite type solid solution loaded with cobalt was synthesized by a pseudo sol–gel method, followed by calcination of propionate precursors. The propionate precursors are synthesised from the metal salts dissolved in the boiling propionic acid, which on evaporation to form gel followed by drying and calcination yielded the fluorite type structure with high micro-homogeneity [196].

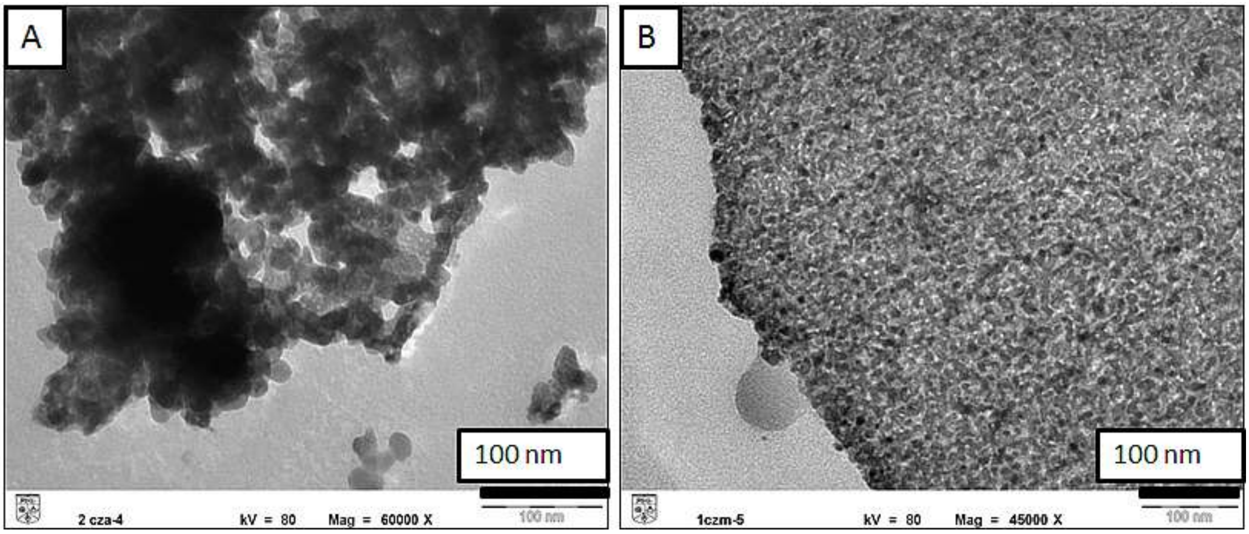

Fig. 1- TEM images of CZ solid solution prepared (a) alone, (b) with citric acid by solid state mixing method

Solid state mixing and anionic exchange method are another methods found in the literatures for the preparation of the CZ solid solution. Atribak et al. [151] reported the simple solid state mixing method for the preparation of solid solution. In this method the nitrate precursors of Ce and Zr are mixed well in a mortar and after that, calcination was done at the desired temperature. The methods were found to the simple and efficient for a large number of catalytic applications including soot combustion. Supported metal catalysts are prepared by the anionic exchange from an acidic solution of metal chloride with the support [197,198]. Fajardie et al. [197] prepared the Rh(Cl) loaded CZ solid solution prepared by the anionic exchange from an acidic solution of $RhCl_3.3H_2O$ at the pH of 1.9 maintained by adding HCl, to the parent CZ solid solution containing nitrate ions even after the calcination procedure. The presence of nitrate ions did not disturb the anionic exchange process. After exchange process, the obtained catalyst samples were filtered, purified and dried.

Polymerised complex or pechini method and high-energy mechanical milling method are the other methods. Kuznetsova et al. [199] reported that the solid solution prepared by the pechini route provides a highly dispersed and homogeneously distributed solid solution with high mesoporosity and sintering resistance to the thermal treatment. Kolkoa et al. [200] reported the same catalyst by same method and established heterogeneity in the solid solution based on the EXAFS study, which revealed the existence of two solid solutions with dissimilar zirconium percentage even though the XRD proved a cubic structure of CZ solid solution. High-energy mechanical milling is a talented technique for the generation of nanostructured phases in the catalysis field. In this method the ceria and zirconia powders or their precursors were mixed with a high-energy vibratory ball-mill at an optimum oscillation frequency of 20 Hz and appropriate amplitude. The precursor powders were loaded with in a high wear-resistant zirconia ball. Trovarelli et al. [70] reported the room-temperature high-energy ball milling for the synthesis of nano phase CeO_2–ZrO_2 solid solution in a large number of compositions.

Other employed methods are solution combustion and flame spry pyrolysis. In solution combustion method, the precursors first mixed withwater in a mortar to form well pasty form. The solution is then cleared with the addition of nitric acid. Finally on calcination of the clear will yield the solid solution [201]. The method is almost similar to the solid state mixing method of the nitrate precursors. Aruna and Patil [202] reported the preparation of nano structured CZ solid solution by the solution combustion synthesis method using some fuels such as carbohydrazide, oxalyl dihydmzide. The as-repared systems provided large surface area and good textural properties with high thermal resistance. During the preparation by combustion method, the light off temperature is significant [41], because it affects the uniformity and reliability of the solid solution and hence a proper segregation is observed [203]. In flame spray pyrolysis method, the organic precursors of ceria and zirconia and metal (if metal is doping) were dissolved in a low boiling organic solvent like xylene. This mixture was then fed in to the nozzle at a particular flow rate with a surrounding O_2 atmosphere, where the combustion of droplets of liquid takes place at the flame around the droplet. The fine particles left were collected and used as the sample without further heat treatment. One great advantage of this method is that the particles are in the nano range in aerosol form. In addition to this, the formed materials found to be fresh catalyst and responsible for the formation of stoichiometric solid solutions. Zhang et al., Madler et al., Teoh et al. and Stark et al. [204-207] preferred the flame spray pyrolysis method for the CZ sample preparation.

Other methods for the preparation of solid solution are hard template method and micro- emulsion method. In hard template method, a mixed solution of inorganic precursors of ceria and zirconia were impregnated into a template and after that the template is removed by a suitable method, which on calcination will yield the solid solution. The samples obtained through this route were observed to be mesoporuos. Lu & Schuth and Watanabe et al. [149,208] reported this method for the mesoporous CZ solid solution. Ghom et al. and Gu et al. [114, 209] prepared mesoporous CZ solid solution using the mesoporous silica as hard template. In the micro emulsion method, a micro emulsion of quantitative solution of ceria and zirconia precursors at a desired molar ratio was prepared with a transparent solution containing the emulsifying components (like CTAB, Butanol, cyclohexene) in specific ratio. Later it was mixed with micro emulsion containing aqueous ammonia. Then both micro emulsions are mixed and stirred to obtain colloidal particles. The residue after aging and on further heat treatment yields the solid solution. Zhao et al., Martinez-Arias et al., He et al. and Liu et al. [174, 210-213] reported the the micro emulsion method.

Non-stop hydrothermal synthesis in supercritical water as antisolvent is termed as supercritical synthesis [214]. In this method, the solution of ceria and zirconia precursors was mixed with supercritical water and heated to obtain the CZ solid solution by the process namely rapid hydrolysis followed dehydration.The prepared systems were found to be nanocrystallites with high homogeneity. Adschiri et al. [215] investigated that by adjusting the pressure and temperature of the supercritical water, the surface morphology and the particle size can be organized. Kim et al. [214,216] investigated the process led for the development of CZ solid solution systems with sparsely-agglomerated morphology, high thermal resistance, high OSC, better reducibility. Wang et al. [217] reported the supercritical drying method for the CZ sample preparation. In this method, to the quantitative nitrate precursors dissolved in water, is treated with ammonia solution for the precipitation. After the completion of precipitation, the residue is kept for aging, and then washed with water or ethanol followed by drying. In supercritical drying method, the residue is dried under supercritical condition in ethanol (265°C and7.0 MPa), followed by calcination will yield the solid solution. Yu et al. [218] reported the nanoporous ceria-zirconia solid solutions prepared trough the high-intensity ultrasonic sound irradiation devoid of any further thermal treatment. The nanoporous particles are formed due to the clustering of mono dispersed nanoparticles by the intense ultrasonic sound. The obtained materials provided high surface area.

Other employed methods are sputtering method [219], colloidal crystal templating method [220], high temperature firing, nitrate glycine gel combustion method [221, 222] and homogeneous gel route synthesis [223,224]. In colloidal crystal templating method [220], the ceria and zirconia precursors were dissolved in a solvent like ethanol and the colloidal crystal template like polymethyl methacrylate was added, followed by mixing and then the resulting composite of ceria-zirconia-PMMA was calcined for the synthesis. The prepared materials are found to be three-dimensionally ordered macroporous CZ solid solutions. This macro pore structure in the catalyst made the system well active for the soot oxidation reaction. Potdar et al. [221] reported the glycine nitrate process (GNP) for the preparation of the solid solution. Here firstly the precursors are made a solution with the glycine. On the evaporation of the excess water it converts to a transparent viscous material, which on drying and calcination will yield the CZ solid solution. This GNP method provided solid solution with high porosity, homogeneity and the system provided high thermal resistance, because the sample doesn't undergone any change in its phase even after calcination at 1000°C. Kapoor et al. [225] reported the deposition precipitation method for the preparation of well-ordered mesoporous Pd/CZ solid solution. The samples obtained through this method were found to possess high surface area and regular pore parameters.

4.1. ***Role of preparation method***

The preparation method greatly influences the properties of CZ solid solution. A large number of studies revealed that the catalytic activities of solid solutions are greatly influenced by the preparation method. The crystallinity, crystal size, surface area and other properties are dependent on the preparation method [226-228]. Here we discussed the effects. Studies by Golunski et al., Liu et al., Tanaka et al. and Tang et al. revealed that co-precipitation method may generate catalyst with high activity and stability compared with the impregnation method in accordance with the large homogeneous distribution of components in the co-precipitation method [229-232]. Yuan et al. [233] reported that the preparation route plays an important role in the catalyst property and the activity. They proposed that through normal precipitation and homogeneous precipitation method, the phase-segregated samples are synthesized but in the micro emulsion method single phase solid solution with superior pore size were obtained. These single phase solid solution played greater role in the stabilisation of the catalyst. Kozlov et al. [234] reported that, the preparation method delivers a characteristic way of interaction concerning the ceria and zirconia, inducing better redox properties upon thermal action. Boaro et al. [235] reported that high surface area is observed for the fresh samples whereas aged/calcined samples have low surface area.

Zhao et al. [174] prepared the solidsolution by four methods. Based on the results, they established that the preparation method and the aging associated with it may play an important role in the properties of the solid solution. All the obtained solid solutions were found to be mesoporous in nature. The solid solution prepared by co-precipitation method showed the largest pore size and pore volume in comparison with the other methods. Pure solid solution samples prepared by the homogeneous and co precipitation method showed both cubic and tetragonal phases; on contrary to this, the cubic phase is shown by the samples prepared by the hydrothermal and the micro emulsion method. Solid solutions by these two methods have better low temperature reducibility and high oxygen storage capacity in comparison with the samples of other methods. They also established that the influence of aging on the catalytic property of solid solutions. Samples after the calcination at high temp showed lower OSC due to sintering of the catalyst by the homogeneous and micro emulsion preparation route. But the aged samples of hydrothermal and co precipitation showed normal low temp reducibility and OSC. They also established that the activity of fresh samples is mainly concentrated on the pore parameter distributions of mixed oxides and the activity of aged samples depends on the redox properties of the mixed oxides. High surface CZ samples (>100 m^2/g) were prepared by the materials obtained from ceria zirconia aerogels [236]. Watanabe et al. [149] reported the formation of highly ordered mesoporous structure through the hard template method. Catalyst prepared by this method will show high surface area and metal dispersion.

Li et al. [237] investigated the influence of preparation method on the cobalt oxide doped CZ solid solution for the three-way catalytic reaction based on the structural and textural property of the samples prepared by co-precipitation and impregnation method. They proposed that the role of cobalt mainly depends on the synthesis method. The doping of cobalt oxide by co-precipitation resulted in the formation of more homogeneous ternary solid solution. A ternary solid solution is that which improves the thermal stability and oxygen storage capacity, which facilitates the promotion of the metal–support interaction and improves oxygen storage capacity at lower temperatures in comparison with the impregnation method. Wu et al. [238] also investigated the influence of preparation method on the catalytic activity and structure of platinum doped solid solution. They postulated that the introduction of platinum in to the CZ solid solution through the sol gel method results in the formation of a nominal solid solution, in which the Pt ions are inserted into the lattice of cubic ceria. But in the impregnation method this type of compound is not observed, Pt is on the surface of the solid solution. The nominal solid solution of sol gel method showed better activity in the exhaust pollutant emission due to the increased oxygen mobility and larger reducibility of the noble metal. The stability of metallic platinum at higher temperatures is responsible for the high activity of catalyst prepared by sol gel method in comparison with the impregnated catalyst. The main reaction takes place in the catalyst is that $Ce^{4+}+Pt \leftrightarrow Ce^{3+}+Pt^{+}$ and oxygen-vacancy diffusion in nominal solid solution. Liu et al. [239] prepared the Pd solid solution by co-precipitation method and the results represent that the Pd^{2+} ions are inserted in to the lattice of solid solution and exhibited a larger activity for the methanol decomposition to synthesis gas due to the small Pd particles on the catalyst. But the impregnated catalyst showed lower activity for the same reaction due to the lack of fine dispersion of Pd particles and low textural characteristics associated with the method.

Huber et al. [173] prepared the Cu doped solid solution by the homogeneous co-precipitation method using urea. The particles are in nano range with high surface area compared with the normal co precipitation method. In this solid solution the Cu and the Zr are randomly spread all over the ceria environment, and there is some CuO like clusters inside the CZ solid solution. These clusters are not formed in the co-precipitation method. Papavasiliou et al. [184] reported the lanthana containing solid solution modified with Pt doped alumina as a three way catalyst washcot prepared by different methods. They showed that the catalyst prepared by co-precipitation method is highly thermally stable compared with the impregnated one. This is due to the well dispersion of the solid solution on the support alumina and hinders the Pt sintering. The solution combustion method is a novel technique for the preparation of nanocrystalline CZ solid solution compared to the other techniques [201]. Wang at al. [217] reported that the structural and textural properties of CZ solid solution are influenced by the drying method. Supercritical drying method results in the absence of vapour–liquid interface in the drying period, resulted to the mesoporous structure of solid solution with an extensive distribution of the pore parameters. The samples prepared by this method also contains larger specific surface area, better thermal stability and higher redox properties and the prominent oxygen storage capacity in comparison with the other drying method which may be due to the enrichment of cerium cations present in the sample and the basic homogeneity in the solid solution. The supercritical drying might reject the vapour–liquid boundary, for the preservation of porous character of the sample [240]. Carla et al. [241] reported the effect of preparation method on the solid solution by two methods, precipitation method (hydroxide precipitates) and firing mixtures of precursors. CZ solid solution formation is detected in the first method, whereas in the firing method, separate mixed oxides are clearly detected. Kozlov et al. [242] investigated the CZ supported on alumina samples prepared by co-impregnation and sol–gel method. They suggested that the samples prepared by impregnation, a ceria rich and a zirconia rich phase were formed instead of the expected nominal solid solution composition. Silva et al. [243] reported the same alumina containing solid solution formation by the impregnation method on contrary to Kozlov et al [242]. Gennari et al. [244] prepared the high surface area, single cubic phase ceria–zirconia solid solution nano particles ($Ce_{0.8}Zr_{0.2}O_2$) by co-precipitation and micro emulsion methods. They postulated that, up on calcination at 600°C, the surface area and pore size were diminished in the two systems, but their crystallite size was increased on calcination. The porosity of the catalysts was found to be lying in the mesoporous range. Kim et al. [214] investigated that the supercritical synthesis generated the sparsely-agglomerated morphology CZ mixed oxides with higher thermal stability and best oxygen storage capacity but the co-precipitation method produced densely agglomerated morphology CZ solid solution. Rhloaded ceria-zirconia catalyst prepared by this method provided higher activity for the NO reduction by CO with better reducibility and thermal resistivity. They also investigated that these catalysts have so many applications as a catalyst related with those by the co-precipitation method.

5. Effect of metal dopants and oxide supports on the CZ solid solution

5.1. *Effect of metal loading*

The concept of metal loading to the CZ solid solution is mainly attributed based on the fact that they have a good capacity to donate oxygen to the metal so the redox behaviour is further enhanced for the reactivity in catalytic applications. Doping elements to CZ solid solution can further improve the thermal stability, as reported by several research groups. In many studies the introduction of transition metals or other rare earth elements into CZ solid solution, promotes the oxygen storage capacity and the redox property at lower temperature [245-254].

Vidmar et al., Minami et al., Ikryannikova et al. and Yucai [255-258] reported that the addition of trivalent metal cations like La^{3+}, Y^{3+}, and Ga^{3+} may stabilise the cubic form of ceria-zirconia solid solution even for high Zr content at higher temperatures. This is mainly due to the well homogeneity acquiredby the CeO_2–ZrO_2 solid solution due to the metal doping. The noble metals like Pd, Pt and Rh etc. loading into the ceria zirconia solid solution were found to be enhancing the reducibility of the solid solution. This concept was experimentally demonstrated by Fornasiero et al., and Ranga Rao et al. [93, 259-261]. CeO_2-ZrO_2 solid solutions containing noble metals were considered as the washcoat materials based on their unique characteristics such as high oxygen storage capacity, thermal stability and enhanced redox and catalytic properties [262-266]. Bozo et al. [267] suggested that electron transfer from the CZ solid solution to the noble metal contributes the generation of a large number of oxygen vacancies due to the low activation energy for the purpose. Or more clearly it should be say that the noble metal may enhance the number of oxygen vacancies and their mobility which results the improved catalytic activity in such systems. Loading of a metal to the solid solution will further facilitate the redox reaction of ceria zirconia solid solution and its catalytic activity is further enhanced by the high OSC and thermal stability [268].

The alkaline group metal especially calcium (oxide) developed an assymmertric strain in the CZ oxide solution, which altered the surface and bulk mobility of oxygen in the solid solution [269]. Inaba and Tagawa [270] proposed a mechanism for this behaviour, as the calcium and strontium ions have the same ionic radii and show a very small association enthalpy between the dopant ions and the oxygen vacancies, which is responsible for the oxygen mobility in the solid solutions. An et al. [271] reported the magnesium doped CZ solution with greater catalytic activity. Sr doped CZ mixed oxide was prepared by both the co-precipitation and impregnation method [170] and discussed that the dopant strontium reduces the sintering of oxide particles in the solid solution and phase segregation during the aging time of the solid solution and revealed the high thermal stability of impregnated one than the co precipitated one, which is due to the well dispersion of Sr particle on the surface and the formation strontium zirconate phase in the CZ solid solution. The catalyst showed better OSC capacity due to availability of plenty of active oxygen species from the strontium zirconate and the ceria zirconia solid solution interface. Adamowska et al. [272] reported the Rh loaded CZ for the selective catalytic decomposition of NO_x to N_2. The metal loaded catalyst provided more conversion with selectivity towards N_2 in comparison with the pure solid solution. In addition to that, the Rh loading reduced the reaction temperature to 34°C in comparison with the unsupported CZ. It is evident from the mechanism predicted by them. Zhao et al. [174] reported the Pd loaded CZ solution by impregnation method. One of the main disadvantages associated with the solid solution alone as a three way catalyst is the deactivation of catalyst due to sintering. They suggested that the doping with Pd shows good activity against the sintering by providing the high thermal resistance to the solid solution.

Watanabe et al. [149] prepared the Ni-Fe loaded solid solution through the hard template method and investigated that the combined metal loading of nickel and iron resulted the formation of an alloy, which further promoted the mobility of the lattice oxygen present in the CZ solid solution and hence a better catalytic activity is noted. A large number of rare earth metals doped or loaded CZ solid solution are investigated based on its application in the three way catalysis [273-282]. Wang et al. [283] reported the properties of solid solution on doping and their catalytic performance in Pd-only catalyst. Wang et al. [282, 283] investigated that the rare earth metals especially Sm, Y, Nd, La, Pr etc. loading will causes the increased surface area of samples and formation of CZ ternary solid solution, in which the some of the Zr ions are replaced by the rare earth metals causing a weaken effect in the sintering property and a high thermal resistance is provided in addition to the increased dynamic oxygen storage capacity. All systems further showed the improved reducibility and strong metal–support interaction. Out of all these, best activities in three way catalysis were provided by the samples promoted with La, Nd, Pr because their strong metal support interaction compared with the other rare earth metals.

Dantas et al. [284] reported the effect of different metal promoters (Pd, Pt, Fe and Ag) on the nickel loaded CZ solid solution. They investigated that Pd and Pt promoters would increase the reducibility of nickel present on the surface of the solid solution, whereas better catalytic activity is shown by the silver promoted one towards the partial oxidation of methane. The solid solution promoted with iron showed small redox property and a small activity in the tested reactions was noticed. The main reason for the addition of metal promoters in the metal loaded solid solution is that they can increase the activity and stability of the catalyst by changing its structural characteristics and will inhibit the coke deposition on the catalyst for a large number of industrial reactions. Also reported that the presence of Ag, Pt or Pd with Ni favours the formation of a metal alloy on the surface of the solid solution while with the Fe promoter, Ni form a metal alloy and the metal adsorbed (Fe) will migrate into the bulk of the solid solution, as reported by Larsen and Chorkendorff [285].

Xiaohong et al. [286] demonstrated the Pd doped Si-modified alumina supported solid solution catalyst. It showed better activity in the methane combustion reaction at lower temp in compared with the silica alumina alone, CZ alone and the both mixed one. The reason for their great activity is that the well dispersion of the metallic Pd particles on the support. Liotta et al. [287] prepared the Pt loaded solid solution supported alumina and the same without the metal for the study of influence of Pt. They demonstrated that the Pt loaded catalyst produced the cubic homogeneous solid solution without the formation of cerium aluminate and well dispersion is noted here, when compared to the non-metal catalyst where the formation of cerium aluminate is detected. The introduction of Pr [288] or Nd [289] into the CZ solid solution lattice showed a larger oxygen storage capacity in comparison with the pure solid solution. The presence of Nd^{3+} and the presence of Pr^{3+} or Pr^{4+} cations in the solid solution promoted the formation of oxygen vacancies, which simplified the oxygen mobility. Zhang et al. [116] reported that the incorporation of Pr into CZ solid solutions largely improves their thermal stability due to the minor kinesis of lattice oxygen resulting from the fusion of Pr and Zr ions into the cubic ceria lattice. Guodong et al. and Trovarelli [290, 4] reported that incorporation of terbium or praseodymium in to the solid solution will increases oxygen desorption at lower temperatures and the generation of oxygen vacancies, which may be due to the lower binding energy of lattice oxygen and the existence of trivalent terbium and praseodymium ions in the solid solution.

Tb loaded solid solutions were prepared by Changgen et al. and Guodong et al. [290,291]. The Tb loading is found to be enhanced the properties of solid solution. Changgen et al. [291] investigated that with increase in the Tb content the surface area were found to be increased in a considerable extent. In addition to this, the Tb allowed to the increased concentration of lattice oxygen and the thermal stability providing a high or better homogeneity in the composition. Uenishi et al., He et al., and Boaro et al. [292-295] reported that the introduction of Y into the lattice of $Ce_xZr_{1-x}O_2$ solid solutions can boost the oxygen mobility and the storage and release capacity. Yang et al. [296] reported the Doping of Nd, which enhanced the thermal stability of ceria zirconia solid solutions. Yuan et al. [233] reported that, up on the Rh loading, ceria-zirconia will improve the oxygen exchange ability of the solid solution and the overall activity of the system towards the auto thermal reformation of methane while these systems have the good trend to the water gas shift reactions. Mei et al. [297] investigated the catalytic activity and thermal resistance of the various metals La^{3+}, Y^{3+}, La^{3+} and Pr^{3+} doped solid solution prepared by the co-precipitation method for the comparison. They established that up on Y doping the specific surface area and thermal stability were enhanced due to the segregation ofY at the crystal boundaries. Doping a small amount of La on ceria-zirconia solid solution can improve the thermal stability. But the specific surface area of La doped ceria-zirconia solid solution decreases with increase in doping amount of La, it may be due to the formation of lanthanum oxide in the lattice of the solid solution. They also investigated that LaCePrZr and LaCePrYZr solid solutions produced by Baotou rare earth mineral residue showed a higher value in specific surface area and showed higher thermal stability.

Zhao et al. [298] reported the Pd loaded lanthana promoted CZ solid solution for the methanol decomposition reaction. According to them, the catalytic activity may be due to the strong interactions between CZ solid solution and the Pd, which exists in two oxidation states (0 and partially positive) and the higher OSC of the solid solution is responsible for the well maintenance of the partial positive charged Pd ion. Terribile et al. [299] reported the Mn and Cu doped CZ solid solution for the oxidation of hydrocarbons. They noticed that the Mn and Cu will dissolve in to the lattice of the CZ solid solution and this will promote the redox behaviour of ceria at lower temperatures. Along with this, some ternary solid solutions are also indicated, due to the presence of zirconia in the solid solution and the metals. The metal doped catalysts provided better catalytic activity compared to the pure CZ solid solution catalyst because of so many ionic defects in the sample generated by the charge compensation route. Jen et al. [300] reported the praseodymia loaded CZ solid solution and demonstrated that which improves the thermal stability of the solid solution instead of the OSC.

Kenevey et al. [130] reported that the noble metals like Pt and Pd dispersion on the homogeneous solid solution enhanced the demixing process. But the existence of noble metal did not have any evident effect on the ceria rich solid solution. They suggested that an interaction between the metal and the support oxide exists which assists the demixing process and enhances the ionic motilities and the noble metals act like a catalyst, by quickening the solid state conversion, but in the case of ceria rich compositions, the noble metal hass no effect on the demixing process. Wang et al. [134] reported that up on Rh loading the surface and the bulk reducibility of the CZ solid solution is upgraded, mainly due to the dissociation of hydrogen and spill over from the Rh into the solid solution. Kimpton et al. and Guo et al. [301, 302] reported that, on Nd doping, the lattice parameters of CZ solid solution is found to become larger than that of the pure CZ solid solution. The provided reason is that, the formation of a ceria–zirconia–neodymia ternary solid solution, causing the expansion of lattice of the solid solution. Wang et al. [303] investigated the effect of Nd doping on structural and textural properties of the CZ solid solution and described that the introduction of Nd into CZ solid solution causes the generation of the ternary solid solution, with enhanced reducibility in addition to the better structural and textural properties and also the better redox nature, due to the migration of Nd from bulk of the solid solution to the surface of the solid solution during the thermal treatment.

Kuznetsova et al. [304] described the incorporation of various transition metals like Calcium, Manganese, Cobalt, Bismuth and Nb for doping and noble metals Platinum for surface modification. They reported that the transition metal doping and the modification by the noble metal cation raise the flexibility and reactivity of both the bulk and the surface oxygen in the CZ solid solution. They investigated the methane combustion over various systems and concluded that the combustion reaction is mainly dependent on the efficiency of the Pt on the doped transition metal oxide. Favourable results are obtained by the systems with high oxygen motilities i.e. mixed with Pt/MnO and Pt/NbO, species on the surface of the CZ solid solution; these systems have the high platinum-support interaction. He et al. [305] described that the incorporation of trivalent Gd into the solid solution increased OSC by creating more oxygen vacancies in the CZ solid solution. Bedrane et al. [306] prepared the noble metals like Rh, Pt, Pd, Ru and Ir loaded CZ solid solution and investigated that the OSC was improved by the existence of mentioned noble metals on the CZ solid solution. But iridium and ruthenium showed best OSC among the other noble metals. The metal particles act as portholes for the successive storage and release of oxygen in the CZ solid solution. Xiaochun et al. and Terribile et al. [307, 308] investigated the effect of Mn doping on the solid solution. They reported the promoting effects of the catalysts in the total oxidation of methane and its combustion respectively. They suggested that the Mn doping will promote the OSC and the catalytic activity. Xiaodong et al. [309] also observed that the introduction of Mn into the CZ mixed oxides promotes the OSC due to the synergetic effect of manganese ion in the ceria lattice and its oxide on the surface. They suggested that a small portion of the Mn are merged into the ceria lattice for the formation of CZ solid solutions and the residual are dispersed on the surface of the system as Mn_3O_4. Vicario et al. [310] reported the gold loaded CZ solid solution prepared through the deposition precipitation and incipient wetness impregnation method. They stated the enhanced effect of the gold in the ceria reduction in the CZ solid solution at low temperature.

There are some studies regarding the Pr doped CZ solid solution. Wang et al. [311] reported the Pr loaded ceria rich CZ solid solution and reported that the Pr enhances the reduction of tetravalent cerium in the solid solution $Ce_{0.66}Zr_{0.34}O_2$ by the oxygen migration to the Pr^{4+} ion. Wu et al. [312] have demonstrated that more oxygen vacancies will be announced in CZ after doping with the praseodymium. Jen et al. [313] noticed the increased thermal stability of the ceria rich CZ solid solution up on the doping of the Pr and the effect also decreased the oxygen storage capacity of the systems. The lower OSC is explained by them as due to the formation of the praseodymia-zirconia system in which the Pr occurred in the +3 oxidation state and which diminishes the OSC. Rui et al. [314] reported that up on the Pr loading a pseudo cubic solid solution was formed irrespective of the zirconia rich composition in the CZ system. Pr prevented the phase segregation during the aging time, enhanced the redox performances in comparison with the pure sample and also enhanced the dynamic OSC. The incorporation of praseodymium into ceria-zirconia could quickens the migration of the oxygen by creating oxygen vacancies, on the zirconia because the Pr is replaced the position of the zirconium. Because of the presence of oxygen vacancies and the homogeneity in the solid solution the oxygen mobility can be promoted through the Pr doping even though Pr ions not participate in the oxide ion transportation. Wang et al. [315] reported the effect of the praseodymium doping on CZ solid solution and the effect on the TWC activity. The studies revealed that the addition of praseodymia results in the formation of Ce-Zr-Pr ternary solid solution in which the Zr ion is replaced with Pr ion, with the special features such as advanced specific surface area, thermal stability and superior OSC than that of CZ.

Sadykov et al. [316] investigated that the addition of fluorine into the CZ solid solution lattice consequences the lower distortion in the structure and as a result of this, the amount of reactive oxygen in the sample is diminished. They suggested that both the calcium ion and the platinum ion addition have the same effect. Adamowska et al. [317] reported the Rh/CZ for the deNO$_x$ reaction. They used both rhodium nitrate and the rhodium chloride for the rhodium loading and investigated that RhCl/CZ catalyst demonstrated lesser NO_x conversion compared to the

RhN/CZ. The provided explanation is that the chlorine ions on the surface of the CZ support hinder the active sites for the catalytic application, whereas the system obtained from the nitrate precursor presented the improved activity with a conversion of 52% at 360°C, may be due to the presence of the Rh_2O_3 and Rh^{3+} phase in the system providing more active sites for the catalytic reaction. Arias et al. [318] reported the CO oxidation over copper oxide loaded CZ solid solution, at lower temperature and low copper loading. They showed that the partially reduced state of CuO and the redox properties on the interface were responsible for the activity of the catalyst. Chen et al. [319] also reported the CO oxidation with the CuO /CZ catalysts, and showed that high activity at low temperature is due to the surface area and small well dispersed and crystalline copper oxide particles in the solid solution. Bozo et al. [132] investigated the effect of MnO on the solid solution and reported that after calcination at 1000°C, the existence of manganese oxide in the solid solution leads to the lack of thermal stability of the solid solution and the generation of new phases and a lowering of surface area are resulted. The calcined catalyst provided no activity in the methane combustion reaction. Minami et al. [320] reported the bismuth oxide and yttria oxide loaded or supported CZ solid solution as an agent for the TWC field, obtained by the thermal decomposition of oxalate precursors by the co-precipitation method. They assumed that the bismuth oxide and yttria will provide the better OSC to the CZ solid solution, due to the formation of oxygen vacancies created by the mobility of oxygen by the substitution of cerium or zirconium ions in the CZ solid solution with the bismuth and the yttria ions, ie.Bi^{3+} or Y^{3+}dissolves into the solid solution. Predominant observation is noticed with the bismuth oxide rather than the yttria doping may be due to the synergistic effect of the easy reduction of Bi_2O_3 and also the tetragonal phase formation which facilitates the oxide migration relatively at lower temperatures.

5.2. *Effect of metal oxide supports*

It is investigated that the support metal oxides have a great role in the properties of CZ solid solution in combination with them. Mei et al. [297] reported that the Al_2O_3 or SiO_2 layer on the surface of ceria-zirconia solid solution increased the specific surface area and thermal resistance to a greater extent but a low OSC value are observed. It indicates that the surface oxides reduced the agglomeration between the particles of ceria-zirconia solid solutions and which is the responsible factor for enhancing the catalyst thermal stability. Silva et al. [321] investigated that CZ on calcination at high temperatures, exhibit very low surface area, and a very little metal dispersion is resulted if metal is loaded. Thus for improving the metal dispersion over the CZ catalyst, other support oxides having high surface are deposited. As a result of this, high metal- CZ interaction is observed with the better catalytic activity. Gao et al. [322] reported that silica supported solid solution has enhanced thermal stability in compared with that of alumina supported one. Arias et al. [323] reported the CZ solid solution containing alumina, prepared by the reverse micro emulsion method. The CZ oxide species are found to be on the surface of the alumina. The EPR spectra of the superoxide ions revealed the aggregated CZ solid solution in presence of alumina in comparison with the unsupported solid solution. Garcıa et al. [324] also supported this behaviour.

Zhan et al. [325] reported the photocatalytic oxidation of benzene using the TiO_2 supported barium doped solid solution. In this catalyst titania is well dispersed on the surface of the barium incorporated solid solution. The solid solution promoted the UV light absorption of the titania in the 210 - 400 nm range than pure titanium dioxide, due to the lower binding energy value of the 2p Ti orbitals. The barium CZ solid solution will give electrons to the TiO_2 and enhanced the light absorption. Using the optimal catalyst they obtained a maximum of 33.9% conversion for the benzene oxidation reaction. Reddy et al. [326] studied the silica supported solid solution. This catalyst showed good activity and selectivity in the alcohol dehydration reaction than the unsupported ones and the catalyst is found to be active for a long time without any deactivation and also at low reaction temperature yielded 50% conversion. The greater activity of the supported CZ solid solution may be due to the well dispersion of the nanocrystalline CZ solid solution on the surface of the amorphous silica.

Xiaohong et al. [286] reported the Si- modified alumina supported CZ solid solution prepared by the reverse micro emulsion method for the methane combustion reaction at lower temperatures with more than 93% conversion. The effect of Si modified alumina CZ solid solution is that, it increased the thermal stability and also promoted the oxygen storage capacity at higher temperatures but the crystalline phases are similar to that of the unsupported solid solution. Pd doped catalyst showed better activity in the methane combustion reaction at lower temperature compared with the Si alumina alone, CZ alone and mixed one because of the well dispersion of the Pd on the support. Kanazawa et al. [327] reported that ACZ solid solution on a nano meter scale for the three way catalysis applications. The introduction of alumina into the solid solution on a nano meter scale was called the diffusion barrier concept [328]. Morikawa et al. reported that the specific surface area of the composite was very high compared with the pure CZ solid solution. This is due to the fact the alumina inhibited the growth of CZ solid solution by inhibiting the growth of pure ceria zirconia solid solution at a high temperature. Fig. 2 depicts the diffusion barrier concept more clearly.

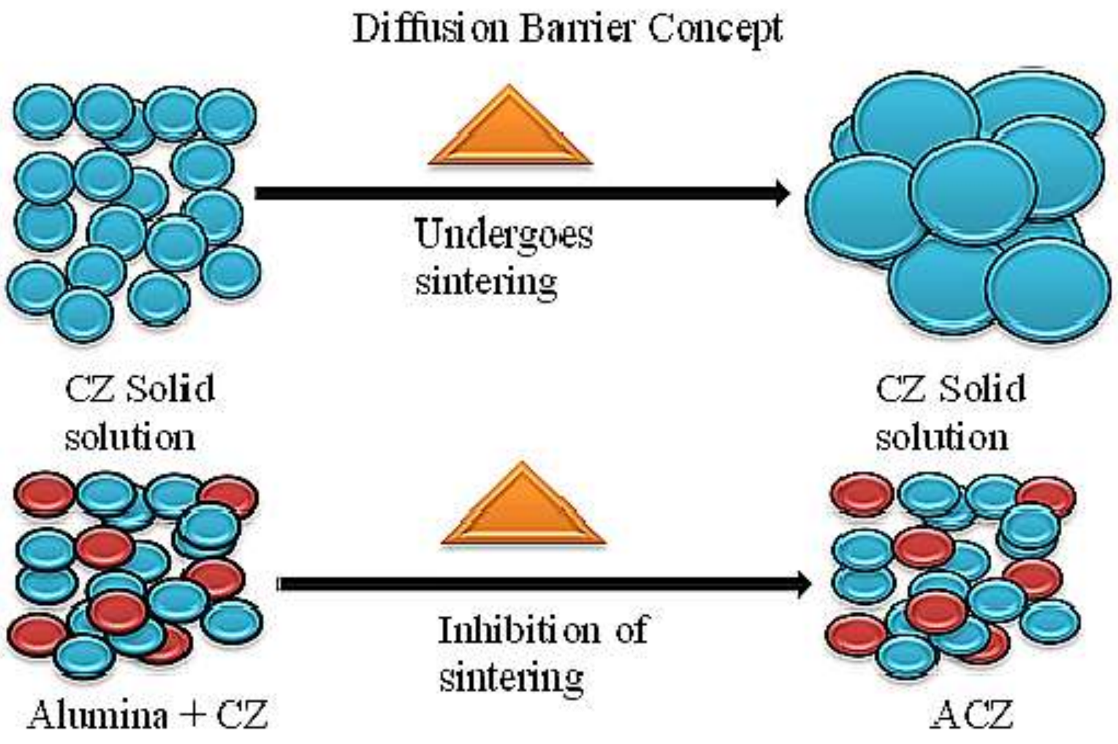

Fig. 2- Graphical representation of diffusion barrier concept

Oxygen storage capacity of CZA were found to be almost same as that of CZ but the release rate is twice than that of CZ in the fresh samples. But after the durability test at 1000°C, the oxygen release rate is five times fast as compared to the CZ. Hosseinpour et al. [329] reported the silica alumina promoted CZ solid solution as a fluid cracking catalyst for the coke combustion and the followed CO oxidation prepared by physical mixing and the impregnation method. The catalyst showed better oxidation property in the above mentioned case, but the catalytic activity of silica alumina for the cracking of 1,3,5-triisopropylbenzene were suppressed by the CZ solid solution. They considered that the better activity in the coke and CO oxidation were attributed due to the presence of active lattice oxygen present in the solid solution. The active oxygen of highly reducible solid solution can decrease CO evolution (by converting it into CO_2) as one of the problems during coke oxidation. The greater deactivation of the catalyst may be due to the strong acidic sites in the catalyst.

Reddy et al. [330] investigated the silica supported CZ solid solution prepared by the deposition precipitation method. The prepared catalysts were found to be nanocrystalline with have a high thermal resistance, surface area and also have high OSC. XRD study revealed the presence of different phases in the system based on the calcination temperature. They observed the presence of two phases at 800°C without the formation of other compounds with silica, ceria and zirconia. The CZ solid solution is well dispersed on the surface of the amorphous silica and reported that there is no increase in the crystallite size is noticed by the increased calcination temperature from 500°C to 800°C, this is due to the influence of the silica support. Hongmei et al. [331] reported the alumina supported CZ solid solution as a good TWC catalyst having many characteristics like large surface area and thermal resistance to sintering, superb reducing ability etc. prepared by the co-precipitation method with an excellent phase homogeneity for a wide range of composition. They suggested that the alumina has an important role in all these aspects of CZ solid solution. Using the CZ alumina system, a large number of reactions are studied. Reddy et al. [332] reported that alumina-supported solid solution display a marked effect on the thermal stability and redox nature of CZ solid solutions over the other supports. Again Reddy et al. [333] indicated that the alumina supported CZ solid solution showed high thermal stability and also the high specific surface area, this is mainly due to the well dispersion of the CZ over the alumina support. The effect of alumina on the CZ solid solution was explained by Sobukawa [87] and reviewed that the CZA have greater specific surface area, smaller particle size, high thermal resistance compared with the pure CZ solid solution. Alumina facilitated the inhibition of the CZ solid solution particle growth and aggregation by the formation of the diffusion barrier layers between the particles.

6. Chemical reactions catalysed by CZ solid solution

A large variety of chemical reactions are reported over the unsupported, metal oxide supported and metal loaded CZ solid solution. The CZ solid solution based catalysis involves mainly the migration or mobility of the oxygen or oxygen vacancies from the surface to bulk or the bulk to surface in the solid solution. Reddy et al. [81] used sulphated CZ super acid solid solution for the synthesis of coumarin under solvent free conditions through the pechmann condensation reaction of phenols with methyl or ethyl aceto acetate. All the tested reactions provided more than 80% yield with good selectivity due to the presence of strong acidic sites in the solid solution. Guodong et al. [82] reported the catalytic activity of the solid super acid for the esterification of lactic acid with n-butanol to the butyl lactate. The esterification efficiency of lactic acid was about 96.6%. Reddy et al. [83] reported the sulphated solid solution catalyst for the synthesis of beta amino ketones in liquid phase through the multi-component mannich reaction at room temperature with high conversion and short duration of time. High catalytic activity for this reaction was attributed due to the acidity of the sample. Yuma et al. [162] investigated the esterification reaction of acetic acid and n-butyl alcohol to butyl acetate over the acidic CZ solid solution and reported that the availability of the proton acid sites and Lewis acid sites in the solid solution are responsible for its activity. The catalyst (2wt %) showed a conversion of 66% under 1:1 mol ratio of acetic acid: n-butanol, within duration of 2.5 hour at the refluxing temperature of n-butanol. Reddy et al. [163] investigated the controlled hydrogenation of the acetophenone to 1-phenyl ethanol over Pd loaded ceria containing solid solution with the alumina, silica, titania and zirconia. The major activity is provided by Pd doped CZ solid solution, due to its well defined structural and textural properties like high redox nature compared to the other catalytic systems.

Sohn et al. [124] reported that the sulphated solid solution super acid catalyst provided a good catalytic activity for two organic reactions, 2-propanol dehydration and cumene dealkylation. Acidity of the prepared catalysts is the factor for the better reaction. They suggested that at an optimum calcination temp of 650°C, the maximum conversion was obtained for both reactions in accordance with the high surface area and acidic sites in the sulphated solid solution. In addition to this 5% cerium sulphate content in the sample showed maximum conversion for both the cumene dealkylation and the 2-propanol dehydration. Further increment in the cerium sulphate content also decreased the activity due to the decreased acidic sites in the sample. Zhan et al. [325] reported the photocatalytic oxidation of benzene using the TiO_2 supported barium doped solid solution. In this catalyst the titania is well dispersed on the surface of the barium incorporated solid solution. The solid solution promoted the UV light absorption of the titania in the 210-400 range than pure titanium dioxide, due to the lower binding energy value of the 2p Ti orbitals. The barium CZ solid solution will give electrons to the TiO_2 and enhanced the light absorption. Using the optimal catalyst they obtained a maximum conversion of 33.9% conversion for the benzene oxidation reaction. Again Zhang et al. [334] investigated the degradation of RhB dye and 2,4-Di-Chlorophenol upon visible-light irradiation over the ceria zirconia solid solution and reported that the trivalent zirconium and tetravalent cerium act as the site for the reduction and oxidation respectively. The solid solution have an Zr^{4+}-O-Ce^{3+} linkage between two tetrahedrons and it showed an optical absorption in the visible region at longer wavelength due to the metal-metal charge transfer of the mentioned linkage. The induced charge transfer in Zr^{4+}-O-Ce^{3+} to Zr^{3+}-O-Ce^{4+} produced a cerium cation and a superoxide anion radical formed by the reaction of oxygen adsorbed and the trivalent Zr ion.

Solinas et al. [335] investigated the dehydrated conversion of 4-methylpentan-2-ol to 4-methylpent-1-ene over the unsupported solid solution. The solid solution introduced good results but they showed low thermal resistance towards sintering. Reddy et al. [326] investigated the same dehydration reaction with silica supported solid solution prepared by the soft chemical route. However this catalyst showed good activity and selectivity than the unsupported ones and the catalyst is found to be active for a long time without any deactivation. Also a lowering in the reaction temperature yields 50% conversion. Reddy et al. [336] reported the same reaction with the solid solution prepared by microwave method and reported high activity and selectivity due to the presence of oxygen vacancies and lattice defects in the sample. They also found that the CZ solid solution is much less active than that of ceria silica catalyst because of the lower acid base property of the CZ compared to the ceria silica catalyst. Yucai [162] investigated the synthesis of butyl acetate from butanol and acetic acid over the ceria-zirconia solid solution using the microwave radiation treatment. Using the 0.5g $Ce_{0.6}Zr_{0.4}O_2$ solid solution, 64.1% conversion of acetic acid was noticed under the mole ratio of acetic acid to butyl alcohol 1:1 during the 15 minutes period with the microwave irradiation. On the conventional heat treatment, 62.2% conversion is obtained for the 4 hour reaction. Deleitenburg et al. [337] investigated the oxidation of isobutanol to isobutene over the ceria rich ($Ce_{0.8}Zr_{0.2}O_2$) solid solution. The solid solution showed better redox property and OSC compared to the pure ceria. Up on the introduction of the zirconia into the ceria lattice, the activity is not changed, but the selectivity to the isobutene is greatly enhanced, this is mainly due to the enlarged oxygen mobility as a result of the formation of surface and bulk defects in the CZ system. Schematic representation of some reactions catalysed by CZ is plotted in Fig. 3 & Fig. 4.

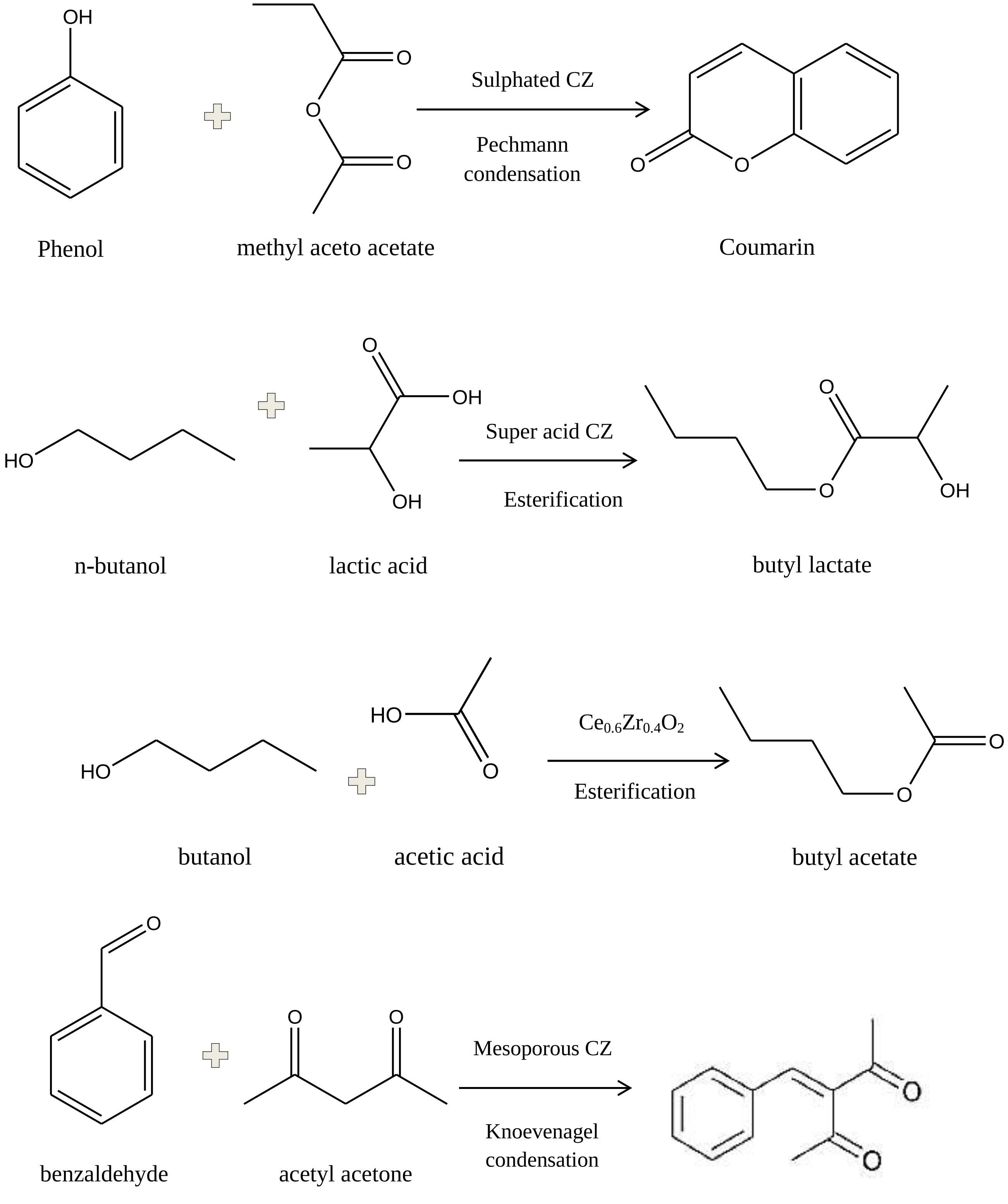

Fig. 3- Schematic representation of organic reactions catalyzed by CZ solid solution

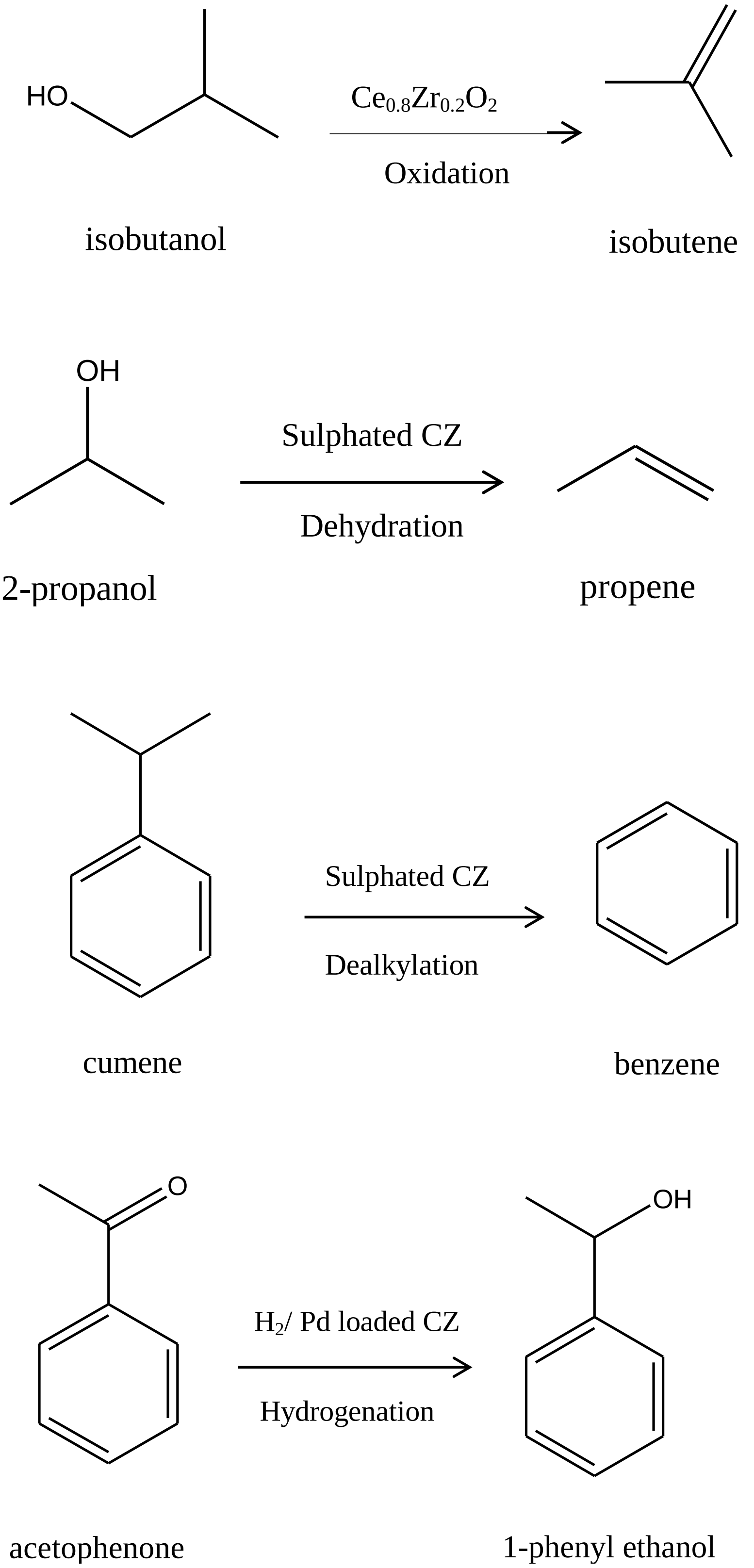

Fig. 4- Representation of some organic reactions catalyzed by CZ solid solution

Zamar et al. [338] investigated the methane combustion over ceria incorporated zirconia system and found that the excellent activity of the catalyst was mainly due to the formation of defective CZ solid solution. Aneggi et al. [339] investigated the oxidation of Landfill Leachate over ceria and ceria-zirconia solid solution and their iron loaded systemby heterogeneous fenton process. Over the mentioned catalysis, all systems have good activity, but best activity is provided by the iron loaded CZ solid solution and it is clear that the CZ system assisted heterogeneous fenton technique can be successfully employed for the oxidative treatment of landfill leachate. Li et al. [340] investigated the wet air oxidation of chlorophenol over the various noble metal (Pt, Pd, Ru) loaded ternary solid solution containing the Ce, Zr and Pr. Among the different systems, Ru system provided better activity at lower reaction temperatures (120^{o}C) and moderate pressures. They studied the effect of pH in this study and established that with increase in the pH of the 2- chlorophenol solution, the dechlorination is improved up to the pH of 6, after which activity was lowered mainly due to the mineralisation of the chlorophenol. Daiz et al. [341] reported the oxidation of hexane, 1,2 dichloroethane, trichloroethylene over CZ solid solution using inverse ion chromatography analysis and reported that for the hexane oxidation, the activity of the CZ system is due to the adsorption capacity of the CZ solid solution. But for the chloroorganics, the specific interaction parameter determines the activity and selectivity, because it is correlated to the oxygen storage capacity of CZ solid solution.

Dantas et al. [303] reported the auto thermal reforming and the partial oxidation of methane over the different metal promoted nickel loaded CZ solid solution. Among the various metal promoters (Ag, Pd, Fe and Pt), silver promoted nickel loaded solid solution exhibited more activity in both reactions. CuO loaded CZ solid solution found active in many reactions. Hu et al. [342] reported the oxidation of volatile organic compounds over the CuO_x /CeO_2–ZrO_2 catalysts. Escribano et al. [343] investigated the propylene oxidation over the CuO loaded CZ solid solution, in which the CuO are well dispersed on the surface of the solid solution. They suggested a mechanism for the oxidation reaction. Firstly, propylene reacts with the CuO surface of the solid solution through pi bonding with carbon-hydrogen at the first position and converted to a propanal species which is then oxidised with the oxygen atoms from the support solid solution to yield the carboxylates (proponoate, acrylate, acetate, formiate respectively) and finally carbon dioxide is obtained. Qingbao et al. [344] reported the ceria-zirconia wash coat loaded with Pd for the toluene catalytic combustion. The monolithic catalyst showed high thermal stability and strong interaction with the substrate and provided a maximum conversion of 97% at lower temperatures towards the toluene combustion, due to the formation of stable PdO phase on the surface of CZ solid solution. Li et al. [345] reported 2 Chlorophenol air oxidation over Ru loaded CZ solid solution. Excellent catalytic activity was shown by these solid solution samples in comparison with the Ru loaded ceria and zirconia. They investigated that the addition of praseodymium and neodymium as promoters improved the catalytic activity. Best activity was provided by the Pr compared with Nd.

Kunkes et al. [346] reported the self-coupling of2-hexanone to form C_{12} compounds along with the minor formation of C_9 and C_{18} ketones and light alkanes containing carbon atoms from 1 to 7 through the two chemical reactions like aldol condensation and hydrogenation over Pd loaded CZ solid solution at high temperatures and pressures. The catalyst consists of an incompletely reducible CZ solid solution, and has acidic and basic properties. They investigated the inhibitory nature of the coupling activity of the compound by the addition of primary alcohols, carboxylic acids, water and CO_2 to the feedstuff. Postole et al. [347] reported the Knoevenagel condensation reaction of a large number of aldehydes and active methylene compounds in liquid phase over the mesoporous CZ solid solution containing nanocrystalline particles prepared through the sol gel method. Best conversion was observed for C/Z-30/70 catalyst with 82% yield within only 50 minutes in comparison with the C/Z (50/50,70/30) catalysts. They suggested that the optimal bifunctional acid-base sites in the catalyst are responsible for the practical implement for promising the catalytic activity in the reaction.

Leitenburg et al. [348] investigated the oxidation of acetic acid in aqueous medium over the CZ solid solution doped with the copper and manganese oxides. They reported that the zirconia incorporation into the ceria lattice would promote the oxidation activity of the catalyst. But best activity in the oxidation reaction is observed for the system, doped with copper and manganese oxides due to the formation of the ternary solid solution and also due to the synergetic interaction between the ceria and the doped metal oxides. The prepared catalysts showed high stability under the applied reaction conditions. Nedyalkova et al. [349] investigated the selective oxidation of methane to formaldehyde over iron doped CZ solid solution. High activity of the catalyst was mainly due to the formation of a ternary solid solution with iron oxide. The incorporation of iron into the CZ solid solution promoted the reducibility of the cerium in the solid solution. The quantity of iron present in the sample determined the selectivity to formaldehyde. Irrespective of the amount of iron present in the sample, only 6% methane conversion was observed for the catalyst.

CONCLUSION

Ceria zirconia solid solution is admirable for its excellent structural and textural properties such as high OSC, surface area, thermal stability and redox capacity comparedto the other catalyst systems. The method of preparation, composition, doping of metals etc. can define the characteristic properties of CZ solid solution. It can be conclude that all characteristics of solid solution can be tuned by the preparation methods, conditions of synthesis, dopants, supports, modifications (chemical filing process) etc. Metal doping is found to have a marked effect on OSC and redox behaviour of CZ solid solution. Sintering resistance is promoted by the presence of silica and alumina supports. In the heterogeneous organic catalysis, mainly in the catalytic reactions, it delivers its enhanced role in various organic transformations. The properties like surface area, pore volume, pore size, thermal and mechanical stability and surface features have been recognised as the vital parameters inducing the increased catalyst activity in CZ solid solution. An overview on the application of heterogeneous ceria-zirconia solid solution in the three way catalysis field for the detoxification of pollutant gases, soot oxidation, hydrogen production technologies, and its role in the oxygen sensors are our subsequent perspective.

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