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Der Pharma Chemica, 2014, 6(1):224-240
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Catalytic aspects of ceria zirconia solid solution: Part-II An overview on recent developments in the heterogeneous catalytic applications of metal loaded ceria-zirconia solid solution

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ABSTRACT

Ceria-zirconia (CZ) solid solution has been considered as a green eco-friendly catalyst and catalyst support for metals. CZ solid solution is admitted for its excellent properties such as high thermal resistance, better reducibility and high oxygen storage capacity. By the incorporation of metals, all the aforementioned characteristics get promoted in a greater extent. Heterogeneous application of metal loaded CZ solid solution is mainly concentrating on the removal of pollutants from the automotive exhaust gas and in the hydrogen production techniques. Metal loaded CZ solid solution exhibits tremendous capability for the simultaneous elimination of hydrocarbons, carbon monoxide and nitrogen oxides present in the auto motive exhaust gas and hence acquired the name "Three Way Catalyst (TWC)". Additionally it plays an important role in the elimination of chlorinated hydrocarbons and in the oxidation of soot. Also it has a marked catalysing effect in hydrogen production from various sources. In this review, we made an outline of the recent developments in the heterogeneous applications of metal loaded ceria zirconia solid solution, mainly focussed on applications in three way catalysis for the removal of several pollutants such as chlorinated hydrocarbons and soot. In addition to this, their application in hydrogen production from different sources is outlined. Their use in oxygen gas sensors is briefly discussed.

Keywords: Metal loaded solid solutions, Catalytic applications, Three way catalysis, Soot oxidation, Hydrogen, Oxygen sensors.

INTRODUCTION

Ceria is one of the most promising rare earth metal oxides, widely used in catalysis either as a single metal oxide or as a mixed metal oxide [1-6]. Among the various mixed oxides of ceria, ceria- zirconia solid solution has got the attention of researchers in accordance with the incorporation of zirconia into the cubic lattice of ceria [7-15], since zirconia has the aptitude to govern the cubic sites of ceria for better catalytic performance [16]. CZ solid solution is admitted for its exceptional characteristics such as high thermal resistance, better reducibility and high oxygen storage or release capacity. The incorporation of zirconia into the ceria lattice raises the oxygen storage capacity in addition to the thermal resistance [17-20]. Therefore, the key catalytic activity of CeO_2 can be accomplished by doping with Zr ions, because of the high redox and high oxygen storage capacity of the so developed CZ solid solution due to the formation physical defects and the rapid diffusion rate of the oxygen atoms present in the lattice [21-38]. The introduction of Zr^{4+} lowers the energy for the reduction of cerium ion and which is responsible for the improved redox behaviour and OSC of the CZ solid solution. Nowadays, ceria-zirconia solid solutions were found to have broad applications in three-way catalysis, heterogeneous catalysts for hydrogen production, conductors for fuel cells etc. Also it delivers an infinite assured performance in various high-tech fields. Some of the zones are in the field of solid oxide fuel cells, gas sensors, steam electrolysis field etc. [39].

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 catalyst activity in CZ solid solutions. It has been established that the addition of Zr^{4+} into the ceria lattice gradually distorts its cubic lattices and the higher zirconium content makes an advanced lattice distortion, therefore altering the crystalline cubic symmetry in to tetragonal symmetry [40, 41]. The high reducibility and improved oxygen storage capacity of the CZ solid solution was mainly due to the presence of structural imperfections, which results in the movement of oxide anions at reasonable temperatures through the lattice sites of solid solution. It is mostly engaged as a director in TWC and activity focuses on the surface and bulk oxygen vacant sites, transaction of the surface oxygen with gas-phase oxygen and the high diffusion rates of bulk oxygen towards its surface. These characteristics are mainly due to the occurrence of the redox couple of ceria in the system [42-46].

In this article (Part-II), we discuss the heterogeneous catalytic applications of metal loaded ceria zirconia solid solution in an energy and environmental point of view. Here we talk over the applications of metal loaded CZ solid solution in three way catalysis for the simultaneous removal of pollutants from the automotive exhaust gas along with the removal of chlorinated hydrocarbons. An outline of the oxidation of soot over CZ solid solution is also provided. Hydrogen production from various sources over the metal doped CZ catalyst is also reviewed in association with the water gas shift reaction. A brief discussion is included on the catalytic application of CZ solid solution in oxygen gas sensors.

2. Metal loaded ceria-zirconia solid solution

The impression of metal doping to the CZ solid solution is credited based on the fact that the CZ solid solution easily donates oxygen to the metal so that its redox behaviour is increased for the catalytic reactivity. The metal doped catalysts provided better catalytic activity compared to the pure CZ solid solution because of the presence of huge ionic defects generated in the sample by charge compensation route. The introduction of transition metals into CZ solid solution stimulates the thermal stability, oxygen storage capacity and redox property at lower temperatures [47-49] or more clearly, the integration of transition metals or other rare earth elements can improve the thermal stability and OSC of ceria-zirconia solid solution [50-56]. Part I of the review discussed the role of metals in CZ solid solution.

Fornasiero et al. and Rao et al. [57-60] studied that the noble metals like Pd, Pt and Rh loading into the CZ solid solution enhances the reducibility of the solid solution and which are considered as the “washcoat materials” with its high OSC, thermal stability and enhanced redox and catalytic properties [61-65]. This is mainly due to the fact that the electron transfer from solid solution to the noble metal generates a large number of oxygen vacancies in the solid solution because of the lower activation energy [66]. Zhang et al. [67] reported that the incorporation of Pr into CZ solid solution improved it thermal stability due to the minor kinesis of lattice oxygen resulting from the fusion of Pr and Zr ions into the cubic lattice of ceria. Guodong et al. [68] reported that the assimilation of terbium and praseodymium into the solid solution increased oxygen desorption at lower temperatures and more oxygen vacancies were created, 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. Wang et al. [69, 70] proposed that the loading rare earth metals especially Sm, Y, Nd, La, Pr increases the surface area of the CZ samples and results in the formation of CZ ternary solid solution, in which the some of the Zr ions are replaced by the rare earth metals causing a decline effect in the sintering property and a high thermal resistance. All systems showed the improved reducibility and strong metal-support interaction. Kenevey et al. [71] reported that the noble metals like Pt and Pd dispersion on the CZ solid solution enhanced the demixing process. But the presence of noble metal ions has no effect in the ceria rich solid solution. They suggested there is an interaction between the metal and support oxide, which assists the demixing process and enhances the ionic motilities; the noble metals acts like a catalyst, by speeding up the solid state conversion, but in the case of ceria rich composition, the noble metal have no effect on the demixing process. Kuznetsova et al. [72] described the incorporation of various transition metals like calcium, manganese, cobalt, bismuth and Nb for doping and platinum for the surface modification. They reported that the transition metal doping and the modification by the noble metal increased the flexibility and reactivity of both the bulk and the surface oxygen in the CZ solid solution.

3. Heterogeneous catalytic applications of CZ solid solution

CZ solid solution is wildly used in industrial applications based on its unique worthy features mentioned in the previous part of the review (Part-I). Here we outlined some of the important applications.

3.1. *Application in Three Way Catalysis*

One of the main problems that we are now facing is the environmental pollution due to the large number of pollutants from various sources. The main source of gas pollutants in atmosphere is from the fuel combustion in automotive exhaust field. Three-way catalysts (TWCs) play an important role in the removal of pollutants from gasoline engine emissions [73-75]. Catalytic systems which decreases the automotive exhaust gas pollutants such as CO, NO and hydrocarbons are termed as the three-way catalysts, they usually comprise three parts namely, a noble metal part, sub-catalyst part and a monolithic ceramic support part like alumina, silica etc.[76,77]. The sub-catalyst part is an efficient catalyst for best results. Removal of gaseous pollutants from the automotive exhaust industry is a challenging task for the topical industries and the ceria-zirconia solid solution and its metal loaded form caught a major responsiveness in this regard and it fulfilled the features of a TWC sub catalyst part. A TWC can simultaneously converts hydrocarbons, CO, and NO present in the pollutant gas mixture from automotive exhausts to H_2O, CO_2 and N_2. The reaction includes the reduction of nitrogen oxides to nitrogen, oxidation of carbon monoxide to carbon dioxide and the oxidation of hydrocarbons (HC) to carbon dioxide and water, as represented below.

$$2\,NOx \rightarrow x\,O_2 + N_2 \qquad (1)$$
$$2\,CO + O_2 \rightarrow 2\,CO_2 \qquad (2)$$
$$C_nH_{(2n+2)} + [(3n+1)/2]\,O_2 \rightarrow n\,CO_2 + (n+1)\,H_2O \qquad (3)$$

The application of CZ solid solution in TWC was firstly investigated by Ozawa et al. [78]. Ceria is the major content in three way catalysts for the elimination of all of the three mentioned pollutants (hydrocarbons, nitrogen oxides, and CO) from automotive exhaust gas [79] based on their redox property [80]. In the TWC, ceria takes the role of an oxygen buffer, or more clearly as an oxygen carrier. Trovarelli et al. [81] reported that the introduction of Zr into the lattice of CeO_2 increases the overall performance of the ceria for the automotive exhaust treatment due to the enhanced thermal stability of the CZ solid solution, because these systems have been considered as the outstanding oxygen storage materials (OSM) in three-way catalysis [82-88]. A simple mechanism for the catalysis in this respect was provided by Wu et al. [89] and explained that CZ solid solution provides oxygen required for the oxidation of CO and hydrocarbons to carbon dioxide and water in the fuel rich condition and it can absorb oxygen for the reduction of NO to nitrogen in fuel lean conditions. They established the potential elimination of pollutants from auto exhaust gas mixture over Pt loaded CZ solid solution.

Wang et al. [90] reported the elimination of CO, CH and NO over the Pd doped CZ- lanthana catalyst prepared by the super critical drying method and the catalyst provided a conversion of 90% with more selectivity with a wide operation of air to fuel ratio. For the representation of the conversion effectiveness in the TWC, there should be an optimum stoichiometric air fuel ratio value, which is normally found to be 14.6. Results showed that Zr-rich CZ mixed oxides has been used as oxygen storage materials in TWC. Here, each of the pollutant from the auto exhaust gas mixture is treated exclusively.

3.1.1. *Nitrogen Oxides (NO)*

Fossil fuel combustion generates a large number of gases, with nitrogen oxides as the major content. One of the important environmental problems is based on this pollutant. Therefore a proper remedy for this problem should be investigated, which is the selective catalytic reduction (SCR) of nitrogen oxides by hydrocarbons [91, 92]. Many catalysts were used for this purpose [93-96], but each of these catalyst systems has its own limitations. Later the activities of CZ solid solution were tested by a few research teams [97-105]. Centi et al. [98] established platinum loaded CZ solid solution with alumina (Pt/ (ZrO_2-CeO_2 on Al_2O_3)) catalyst for the reduction of NO by propene. They suggested a low temperature reaction when the catalytic system is reduced with hydrogen at 800^0C; after that a mild re-oxidation is necessary for the low temperature reaction. They proposed that oxygen vacancies created by the high metal support interaction is the responsible factor for the best catalytic activity [99]. Liotta et al. [99] reported NO reduction by the propene over 1% Pt loaded CZ under the fuel lean conditions. They postulated that improved catalytic activity was observed when the catalyst was reduced with hydrogen at 350°C.But the reduction pre-treatment at higher temperatures (800°C and 1050°C) showed a diminishing activity. The different catalytic analysis proved the existence of a strong interaction between the Pt metal and the CZ support. This feature is responsible for the lower reduction temperatures of the systems. Thomas et al. [100] reported the influence of Pd loaded CZ solid solution on the SCR of NO by propene. The prepared catalysts showed better selectivity towards the nitrogen gas (>80%) and proposed a lean deNOx mechanism for the reaction which is different from that by the Pd doped silica. The reduction of NOx aided by propene over Pd, Rh, and Pt noble metal loaded CZ solid solution catalysts was studied [101] and compared the same with silica and alumina supports. They showed that the reactivity of the systems were found to be Pd >> Pt ≥ Rh in addition to the excellent selectivity shown by the CZ solid solution compared with silica and alumina, the provided explanation is based on the mechanism predicted previously. The greater activity of the Pd catalyst is due to the high capability of the PdOx species to adsorb NO_2 in comparison with the other oxide species of Rh and Pt. They studied that the greater interaction of the PtOx and RhOx species with CZ, therefore they have a lower power to absorb the NO_2 gas.

Mariadassou [102] reported a mechanism for the deNOx reaction. Firstly, oxidation of NO into NO_2 takes place at the CZ support or by the loaded metal oxide. In the second step, the produced NO_2react with the hydrocarbons and liberate R-NOx species along with the CxHyOz species, this step takes place on the surface of the metal oxide. Final step is the reduction of NO by decomposition by the CxHyOz species to produce nitrogen. This step takes place on the catalyst support. Ferreira et al. [104] explained the same mechanism. Gorce et al.[105] also suggested that the generated intermediates in the reaction will reduce the CZ solid solution very easily and results in the formation of active sites for the reduction of NO to N_2.

Adamowska et al. [92] reported the effect of Rh loaded CZ solid solution for the SCR of NOx by a variety of aromatic and aliphatic hydrocarbons. They concluded that the activity of catalyst increases with the ceria content. The Rh loaded catalyst yielded 57% conversion and lowered the reaction temperature to 34°C. They proposed a hydrocarbon assisted mechanism for the catalytic reduction involving three steps, as described earlier. The proposed mechanism was in agreement with some research teams [102-104]. Zhang et al. [106] reported the SCR of NOx by CO using the copper loaded CZ solid solution prepared by spray pyrolysis method. They established that, in comparison with Cu/CeO_2, Cu loaded CZ solid solution showed strong interactions between Cu and Zr providing high Cu^+/Cu^{2+} ratio, where NO chemisorbs on Cu^+ and causes high surface oxygen mobility, which is more active than the corresponding copper loaded zirconia. This is due to the effect of the solid solution formed. Two mechanisms are suggested for this reaction. One is the dissociation mechanism occurring at a lower temperature of 250°C. It involves the reductive chemisorption of NO on the Cu^+ sites and the oxygen vacancies created by the reductive trivalent cerium ions will convert the NO to N_2O. An organonitrogen mechanism is suggested at higher temperature, since there is no formation of N_2O.

Liotta et al. [107] reported the NO reduction by propene over Pt/ceria–zirconia/alumina catalyst. The catalyst provided good NO conversion (55%) and selectivity (50%) at lower reaction temperatures. Adamowska et al. [108] reported the deNOx reaction by the hydrocarbons mixture containing toluene, propene and propane over the CZ solid solution. They proposed that there are three sites for chemical adsorption of NO on the surface of the solid solution based on the fact that there are three NO desorption peaks in the TPD result and considered that these sites are altered units of the support unsaturation due to the other oxidation states of cerium ion. The three active sites are (1) completely oxidised support, (2) partially reduced system cation, (3) completely reduced system cation and reported the nature of surface species formed on the absorption of NO by the diffuse reflectance fourier transform infrared spectroscopy. They observed that at room temperature, nitrite ions are formed on the catalyst surface and at moderate and very high temperatures, nitrites and nitrates are formed on the surface of CZ. The nitrites are converted to nitrates as temperature increased and discharges NO and NO_2 respectively. The ceria–zirconia solid solution was found to be active in presence of present hydrocarbon mixture [109].

Letichevsky et al. [110] studied the NO reduction by CO with additional molecular oxygen over the Pd loaded CZ solid solution ($Ce_{0.6}Zr_{0.4}O_2$). The catalyst provided 100% selectivity to N_2. They found that reaction temperature has a role here because at temperatures lower than 200°C, NO reduction takes place while at higher temperatures (>200) CO oxidation takes place. The provided mechanism is that, firstly, the NO species are adsorbed on the surface of the metal and decomposed to form active adsorbed nitrogen and oxygen intermediates [111, 112]. The active N intermediate combines with the NO and liberates N_2 and active oxygen, which on reaction with the CO, produces CO_2. At lower temperatures, the active species have no energy to take part in the CO oxidation reaction so 100% selectivity is noted, while at higher temperatures there is a possible competition between the two reactions such as NO reduction and CO oxidation. Wang et al. [113] studied the catalytic reduction of NOx over the Nd doped CZ solid solution and reported that the higher OSC generated by the Nd loading provided the exact reason for the better conversion of NOx which is mainly due to the oxygen vacancies associated with the trivalent cerium ions adjacent to the Nd noble metal as reported by Vidmar et al. [114] and Rao et al. [115].

Hurtado et al. [116] investigated the NO oxidation over CZ solid solution with ceria rich compositions using different ceria precursors. They proved that both catalysts show a minute difference in the reaction. Instead of the sample prepared from Ce^{3+} precursor, ammonium cerium nitrate precursor catalyst showed much more activity. This is mainly due to the different Ce/Zr surface ratios and better reducibility of the catalyst. Atribak et al. [117] studied the NO oxidation over the CZ solid solution obtained by co-precipitation method and reported that the surface composition of the catalyst plays an important role in the reaction. They proved that solid solution containing cerium-rich surface, with high Ce/Zr atomic surface ratios, are found to be more active than the zirconium rich surface of the solid solution and established that the surface area have a minor role and the Ce/Zr surface ratio play the major role in the NO oxidation reaction in agreement with Hurtado et al. [116].

3.1.2. *CO oxidation*

Other important three way catalytic application of CZ solid solution is the CO oxidation. Boaro et al. [118] reported the carbon monoxide oxidation over a series of fresh and aged CZ solid solutions. The catalytic activity of all fresh samples were found to be depend on the redox sites of the exposed surface, but that of the aged samples depend on the surface area of the catalyst. Liotta et al. [107] investigated the CO oxidation using the Pt/ CZA catalyst with better conversion and high CO_2 selectivity at lower temperatures and which may be due to the well dispersion of Pt on the surface of CZ solid solution along with high oxygen mobility. Thammachart et al. [119] investigated the CO oxidation over the CZ solid solution prepared by the sol- gel method. They proposed that Ce/Zr ratio of the solid solution plays an important role in the CO oxidation activity, because it is related to the degree of reducibility of the catalyst. With lower Ce/Zr ratio, the lower CO oxidation is noticed due to the phase composition difference of the catalyst. Among a set of catalysts, ceria rich catalysts proved to be the best one for CO oxidation. Reason is that the cubic phase CZ solid solution suits in a great extent for the CO oxidation rather than the tetragonal phase. Reddy et al. [120] investigated the CO oxidation over ceria mixed oxides prepared by the microwave method. Among the ceria solid solutions of alumina, silica, zirconia, and titania, ceria zirconia mixture provided the best CO oxidation result due the formation of homogeneous CZ solid solution with high OSC and reported that introduction of zirconia into the ceria lattice promoted the formation of defective sites which is responsible for the best CO oxidation activity.

Arias et al. [121] reported the CO oxidation by NO in presence of CuO/CZ, at lower temperature and low copper loading. They noticed that the partially reduced state of CuO and their redox properties on the interface are responsible factors for the activity of the catalyst. Chen et al. [122] reported the CO oxidation over CuO/CZ catalysts and showed that high activity at low temperature was due to the high surface area and well dispersed nanocrystalline copper oxide particles in the solid solution. Singh and Hegde [123] reported the CO oxidation with ceria containing solid solutions and suggested that the CZ solid solution have lower activity than the ceria solid solution with iron, in accordance with the large OSC of this system compared to the CZ solid solution. Wang et al. [124] reported the CO oxidation over Rh loaded CZ solid solution and established that CO oxidation activity of the cubic solid solution is relatively more than for the tetragonal and monoclinic phases of CZ, which may be due to the low reducibility of the system. The provided explanation for the highest activity of the cubic phases may be due to the enhancement of rhodium dispersion in the ceria rich solid solutions. Reddy et al. [125] investigated the CO oxidation over the ceria zirconia and ceria terbia solid solutions and their alumina supported forms. The order of the catalytic activity of the systems were found to be alumina- supported ceria-zirconia > ceria-zirconia. But the CZ system showed lower effect compared to the ceria terbia systems. For CZ systems, maximum CO conversion was observed after 477°C. The decreased activity of the CZ systems were mainly due to the lower number of redox sites in those systems instead of the OSC.

Wang and Valenzuela [126] reported the CO oxidation over the Pd loaded solid solution and established that among the various catalyst tested, 3% Pd doped ceria rich solid solution have the highest activity with a light-off temperature 120^{o}C for CO oxidation. Caputo et al. [127] investigated the CO oxidation in hydrogen rich gases over the copper oxide loaded ceria and CZ solid solution and reported that the zirconia incorporated on the ceria have no effect in the catalytic performance in CO oxidation. The 5 % CuO/ceria catalyst have greater activity with a light-off temperature of 70°C. At higher temperatures, hydrogen begins to oxidise resulting the maximum conversion of CO. Bharali et al. [128] reported the CO oxidation over the noble metal doped (Hf, Pr and Tb) CZ solid solutions. They found that the Tb loaded CZ solid solution experiences higher reduction compared to the Pr and Hf loaded CZ solid solutions. They indicated that the redox couple of the dopant metal and the calcination temperature have a great role in the CO oxidation. For this reaction, best catalysts were found to be Tb loaded one calcined at 500°C and Pr loaded one at 800°C with respect to the equilibrium CO conversion (50%).Martorana et al. [129] studied the anaerobic CO oxidation over the Pt loaded CZ solid solution. They suggested that the CO oxidation accompanied by the reduction of the catalyst support due to the intake of the surface oxygen, which is a slow process and provides an initiation time, but the bulk reduction, can be done very fastly. The metal support interaction will affect the induction period and regulates the electronic properties of the catalyst. With increase in the octahedral lattice site oxygen, more exchange will take place and the bulk to surface diffusion rate will be faster than desorption of the carbon dioxide produced by the CO oxidation process.

Gomez et al.[130] investigated CO oxidation over the Au loaded CZ solid solutions and reported that C/Z ratio, OSC and reducibility power of the solid solution were responsible for the increased activity of the support for gold nanoparticles in CO oxidation. The better catalytic activity was mainly due to the synergetic effect between the CZ solid solution support and gold particles at the catalyst interface. The CZ solid solution acts as a buffer in oxygen liberating and up taking process. They also reported that the gold loaded ceria and solid solution have almost same activity at lower reaction temperatures and also at room temperatures. Boaro et al. [131] investigated the CO oxidation in steady state conditions over the various compositions of fresh and aged CZ solid solution in anaerobic conditions both in the pulse mode and also in the cycling mode. Under the steady state conditions, zirconia has no effect in the CO oxidation and high activity was shown by ceria samples. The major catalytic activity of the CZ solid solution at lower temperature was noticed when the reaction was carried under the transient pulse mode. The reason for the best catalytic activity under these conditions is due to the active reducibility power and the high oxygen storage capacity of the ceria-zirconia solid solution. The enhancement of catalytic activity in the respect was mainly due to the higher bulk diffusion rate of ceria–zirconia solid solution.

3.1.3. *Elimination of chlorinated hydrocarbons*

One of the major air pollutants that now we are facing is the chlorohydrocarbons which are highly stable, toxic and are emitted by various industrial areas. Therefore a special care is needed for the destruction of these compounds. CZ solid solution finds a virtuous role in the elimination of chloroorganics. Rivas et al. [132] introduced the CZ solid solution for the oxidation of chlorohydrocarbons to CO_2 and HCl and with minor amounts of chlorine gas. For the oxidation reaction, they selected trichloroethylene as the chlorine source and the reaction was conducted in gas phase over CZ solid solution prepared by the precipitation method. Among the various catalysts prepared, most acidic catalyst with high zirconia content showed the higher activity which is mainly due to the availability of lattice oxygen. The formation of Cl_2 gas is limited by this catalyst. They suggested a mechanism for the dechlorination reaction. Initially the trichloroethylene gets adsorbed on the surface of solid oxide catalyst followed by the insertion of oxygen from the CZ, resulting in the formation of mono chloroacetate. After that chloride ion abstraction takes place for the formation of acetates, which then oxidatively decomposes to CO_2. This mechanism was in agreement with that predicted by Jeurissen et al. [133].

Rivas et al. [134] performed the decomposition of 1, 2-dichloroethane over a wide composition of pure CZ mixed oxide catalysts because of their promoted redox and acidic properties; a catalytic activity change with the zirconia content was observed for the samples. Highly homogeneous catalyst $Ce_{0.5}Zr_{0.5}O_2$ showed a better performance. The proposed mechanism involves 1,2-dichloroethane dehydrochlorination by the presence of acidic sites of the catalyst to form vinyl chloride after the removal of HCl. Then the vinyl chloride gets protonated in the presence of basic surface species (OH), which results in the formation of carbonium ions. These ions are trapped by the nucleophilic oxygen from the catalyst to form chlorinated alkoxide compound. It decomposes to yield acetaldehyde, finally which converts to CO_2 with trace amounts of CO. This mechanism is based on the in situ FT-IR spectra studies. Again Rivas et al. [135] investigated the oxidation of chlorinated hydrocarbons such as 1,2 dichloroethane and trichloroethylene over a series of CZ solid solutions in both single state or in a mixture with toluene and reported that the surface acidity of the catalyst and the availability of its lattice oxygen is responsible for the well oxidation of chlorohydrocarbons. Higher oxidation is observed for the dichloroethane compared to the trichloroethene. Toluene has a significant role in the mixture feed because it enhanced the catalytic activity and selectivity. The concurrent oxidation of the chlorohydrocarbons with toluene caused major changes in both the activity and selectivity in the present reaction. The best catalyst systems for this reaction were found to be zirconia rich system with weight percentages 50 and 85%. Rivas et al. [136] reported the oxidative decomposition of dichloroethane over a series of sulphated CZ solid solution, prepared by using 1M aqueous solution of the sulphuric acid and nitric acid. The superior catalytic activity was due to the increased acidity of the CZ solid solution. It lowered the reaction temperatures to 80°C and 120°C for the oxidative decomposition of the dichloroethane. They concluded that the sulphation of the CZ solid solution was an active implement to develop the performance of CZ in the chlorohydrocarbons elimination. Li et al. [137] reported the catalytic wet air oxidation of 2-chlorophenol over Ru loaded CZ solid solution at lower reaction temperatures and pressures. The enhanced activity of the catalyst was mainly due to the redox properties of the solid solution, which promotes the migration of the lattice oxygen to the active catalyst sites.

Ortiz et al. [138] investigated the oxidation of dichloroethane and trichloroethylene over CZ solid solution and indicated that the catalyst showed much higher activity than the pure ceria and zirconia and the activity of the catalyst in this respect depended on the Ce/Zr molar content. Along with the major oxidation products such as CO_2, HCl and chlorine; trace amounts of vinyl chloride and tetrachloroethylene and CO were detected. With increasing the ceria content, carbon dioxide and chlorine were formed through the deacon reaction. Again Ortiz et al. [139] investigated the oxidation of chlorinated organic compounds like dichloroethane, trichloroethylene in presence and absence of n-hexane over CZ mixed oxide catalyst. The activity of the catalyst for the oxidation of chlorinated organics depended on the ceria/zirconia molar ratio, surface acidity and the OSC of the CZ catalyst. Homogeneous solid solution showed activity in the abatement of chlorohydrocarbons, but ceria is well active for the oxidation of non-chlorinated organics. In presence of n-hexane, an increase in the ignition temperature is noticed. Increase in HCl selectivity in the reaction may be due to the mixture effect, generated by the addition of n-hexane which produces water by its combustion process and the water formation is responsible for the increased selectivity to HCl.

3.2. *Application in soot oxidation*

Soot particles from diesel engine outlets are very hazardous materials and which reasons a severe natural pollution that primarily affects the biosphere. In order to overcome the limitation of alternative regeneration of the diesel particulate filter by the deposition of particles, CZ solid solution was efficiently used. Ceria is considered as a powerful soot oxidation catalyst [140,141]. But it is well known that during the soot oxidation with oxygen, a huge amount of heat is liberated according to the exothermic nature of the reaction and the measured heat was found to be about in the range of 1000°C-1100°C [142]. At this temperature ceria is not a good catalyst because of the lack of surface area and OSC. Therefore CZ solid solution finds a virtuous role in this application in accordance with its high temperature stability [143-147]. Krishna et al. [144,145] reported the soot oxidation using the ceria modified with the La and Pr in presence of oxygen and a mixture of NO and O_2in the tight and loose contact. They explained that the calcination of the catalyst has an important role in the crystalline size and surface area of the system for the soot oxidation. Greater activity of the catalysts was mainly due to the stabilisation of the catalyst in terms of their surface area and redox property. Among La and Pr, the praseodymium doping provided the best activity with oxidants, O_2 and mixture of NO and O_2, and established that the NO oxidation was found to be high over the praseodymium-doped catalysts.

Aneggi et al. [148] reported the diesel soot oxidation mechanism over CZ solid solution both in the presence and absence of oxygen and explained the surface and bulk oxygen properties of the CZ catalyst. At lower temperatures, the soot oxidation takes place with the active oxygen present on the surface of the catalyst, (absence of gas phase oxygen) and these oxygen vacancies are refilled by oxygen conditions or from the bulk of the catalyst. In the absence of gaseous oxygen, the amount of ceria in the composition decides the activity. But in the other case, OSC of the material plays the primary role. The two steps co-exist during the whole reaction with some additional factor i.e. soot-catalyst contact. Thrimurthulu et al. [149] investigated the soot oxidation over the ceria-praseodymia and ceria-zirconia solid solutions and reported that the ceria–praseodymia catalyst presented high catalyst activity compared to the CZ solid solution. This is due to the better availability of lattice oxygen and redox sites in the former solid solution with respect to the CZ solid solution. Reddy et al. [150] investigated the soot oxidation over the ceria, ceria-zirconia and ceria-hafnia solid solutions and reported that the oxidation of soot was upgraded by the insertion of zirconia and hafnia into the cubic ceria lattice. The better activity was shown by the ceria-hafnia in comparison with the CZ solid solution. High activity of the hafnia solid solution is mainly due to the ease of availability of lattice oxygen. They also explained a simple mechanism for the soot oxidation. The lattice oxygen from the catalyst or the gas phase oxygen reacts with the soot particles which results in the generation of CO adsorbed-soot particles and they are treated as the carbonates. In presence of the gas phase oxygen, the catalyst re-oxidation takes place with the simultaneous decomposition of the carbonate into carbon dioxide. Reddy and Rao [151] reported the soot oxidation in tight contact condition over mono metallic CoO loaded and NiO loaded CZ solid solution and the CuO promoted bimetallics of the above catalysts. All the catalysts provided better activity, but among them, the CuO promoted CoO CZ solid solution showed the best activity and 100 % selectivity to CO_2. This is also due to the formation of a solid solution of ceria and copper oxide and also due to the crystalline spinal phase formation. In addition to this, oxygen vacancies, nano size of the metal particles and their surface area are also responsible for the better activity towards soot oxidation.

Katta et al. [152] reported the soot oxidation over pure ceria, CZ and CL solid solutions. They discussed that the CL solid solution provided more activity compared with ceria and CZ, based on their high OSC and thermal resistance in comparison with the ceria and ceria-zirconia solid solution. Zhang et al. [153] reported the diesel soot oxidation over the Pr modified CZ solid solution prepared by the colloidal crystal templating method. The catalyst is three-dimensionally ordered, macroporous and showed better activity in the soot oxidation in comparison with disordered microporous catalyst. The better catalytic activity of solid solution is mainly due to the efficient contact between the ordered catalyst and the diesel soot. Aneggi et al. [154] reported the diesel soot oxidation over CZ solid solution and the rare earth metal (La, Pr, Sm and Tb) doped CZ solid solution. They showed that the CZ solid solution doped with rare earth does not provide the lower temperature soot oxidation combustion as like undoped CZ solution. The rare earth dopants introduced in ceria-zirconia solid solution promoted the thermal stability; but here some other variables played a major role in the catalytic activity such as preparation method, textural and structural properties. Sullivan et al. [155] studied the soot oxidation over the CZ solid solution by the in-situ Raman spectra method. From the results they concluded that catalyst has the capacity to transfer oxygen from the catalyst surface into the soot, resulted the formation of CO/CO_2.

Atribak et al. [156] investigated the soot combustion over yttrium loaded ceria and ceria rich CZ solid solution and reported better result in CZ solid solution both in loose and tight contact condition. They reported that, in loose contact condition, the surface area of the catalyst plays an important effect on the soot combustion and established that the CZ-yttria comparison with the yttria loaded ceria have the prominent activity. But in tight contact condition, ceria yttria is the most active catalyst in comparison with the CZ-Yttria solid solution. In the case of the mixed oxides, the influence of zirconium on the soot combustion activity disables to that of yttrium, since ceria is the active participant in the reaction. Oliveira et al. [157] also reported the diesel soot oxidation over a wide composition range of CZ systems prepared by the sol gel route. They proposed that among the various systems, the ceria rich ($Ce_{0.8}Zr_{0.2}O_2$) system showed highest activity and it shifted the soot combustion temperature from 622°C to 547°C and 404°C, both in loose and tight contact respectively and the system is found to be resistant to deactivation up to five consecutive runs. Escribano et al. [158] investigated the application of Mn_2O_3 oxide loaded CZ solid solution for diesel soot oxidation. They established that combustion of the mixed soot and the catalyst takes place in the range 147°C-447°C and FTIR study revealed the presence of some carboxylic species as intermediates. The soot oxidation reaction is more selective to CO_2, with traces of CO as by-product; its extent can be decreased by increasing the feed of oxygen.

3.3. *Applications in hydrogen production*

Hydrogen is the remarkable energy transporter in coming years due to the increased utilization of fossil fuels. In addition to the automotive exhaust catalysis, pure and metal doped CZ solid solution found applications in the hydrogen generation. CZ solid solution has caught the attention in hydrogen production technologies especially in the reformation of alcohols and combustion of natural gas. The applicability of CZ catalysts in this regard was mainly due to the unique commendable features described earlier. A large number of reports are available for the production of hydrogen and syngas from methane by partial oxidation method over Pt loaded CZ solid solution catalysts [159-165]. The high catalytic activity was attributed due to the high reducibility and OSC capacity of $Pt/CeZrO_2$ catalysts. These features are responsible for the removal of coke from the active catalyst sites and hence a best catalytic activity was resulted. Duhamel et al. [166] investigated the hydrogen production from methane at low temperature over nickel loaded CZ solid solutions, in presence of O_2. At a high temperature of 650°C, 100 % hydrogen yield were obtained and at lower reaction temperatures like 200°C, 34% yield was obtained with a conversion of 53% and H_2 selectivity of 64 %. Yuan et al. [167] reported the auto thermal reformation of methane for the production of hydrogen over rhodium and magnesium oxide promoted CZ solid solution. In all catalysts, 99% conversion of methane with high selectivity was noticed. The stability of the catalyst was due to the interaction between ceria-zirconia, MgO promoter and the active component Rh. Greater H_2 selectivity is attributed to the high WGS activity of the mixed oxide solid solution. Silva et al. [168] investigated the production of H_2 rich syngas by the partial oxidation of methane over the Pt loaded CZ solid solution supported with alumina. Better results are obtained by these systems with high metal loading. Even though the CZ content increases, the selectivity towards H_2 is decreased; this may be due to the high OSC of samples. They also put forwarded a mechanism in agreement with Dissanayake et al., Ashcroft et al. and Looij et al. [169-171]. In the first step, methane undergoes oxidation to form CO_2 and H_2O and in the second step, synthesis gas is formed from the CO_2 and the steam reformation of unreacted methane takes place. In the partial methane oxidation, better catalyst stability and the selectivity were observed for the Pt loaded CZ alumina catalyst, due to the higher metal and CZ interactions with the additional influence of alumina [168, 172]. Terribile et al. [173] investigated the hydrogen production from the various light hydrocarbons oxidation over Mn and Cu doped CZ solid solution. The better hydrogen production activity is provided by both catalysts with high selectivity and conversion at low temperatures, which is mainly due to the oxidation ability of the metals and their redox property at lower temperatures along with the high catalytic properties of the CZ support.

There are many catalysts, that had tried for CO_2 reforming of methane to produce syngas by using metal oxides and metal doped oxides but large sintering is noticed. Later, the application of CZ solid solution in this field was studied. Noronha et al. [174] investigated the CO_2 reforming of methane over Pt loaded CZ solid solution to obtain syngas. The catalyst showed better reducibility and good conversion for a long duration of time without any deactivation. They proposed a mechanism for this reaction. The first step involves decomposition of methane molecule on the metal surface producing hydrogen and carbon, then the carbon get deposited on the metal surface which further reacts with the oxygen from the support or oxygen formed by the dissociation of carbon dioxide and forms CO. Xu and Wang [175] investigated the catalytic activity and stability of Ni loaded CZ catalysts for the partial oxidation of methane to produce syngas [176]. Larrondo et al. [177] investigated the same for the partial oxidation of methane for hydrogen production with the liberation of CO and established that CZ solid solution act as a good catalyst in this reaction at low oxygen atmosphere indicating that the lattice oxygen present in the solid solution take part in the reaction. Larrondo et al. [178] investigated the improved effect of nickel loading in the CZ catalyst, but the effect was found to be temperature depended. At lower temperatures, total oxidation of methane to water and CO_2 were investigated. Due to the non-reduced nickel sites in the catalyst and at higher temperatures (>650°C), the catalyst resulted in the partial oxidation reaction with the theoretical ratio of (H_2/CO) products as 2.

Kusakabe et al. [179] investigated the methane steam reformation over noble metal loaded Ni/ CZ solid solution. They established that, 10% Ni loaded CZ showed highest methane conversion to syngas at 500°C–600°C and a high H_2/CO ratio was observed which was mainly due to the water-gas shift reaction and reported that activity was further upgraded by loading with Pt, Ru and Rh. The highest catalyst activity was provided by Rh system. Halabi et al. [180] investigated the steam reformation of methane over $Rh/Ce_{0.6}Zr_{0.4}O_2$ catalyst at low temperature range for hydrogen production. At higher temperatures, there is a considerable inhibition in the formation of H_2, CO, and CO_2 and which reduced the methane conversion. They explained a molecular mechanism as follows. Firstly the dissociative adsorption of methane takes place on the catalyst-support surfaces. Then methane is adsorbed by dissociation in the rhodium metal site and the steam is dissociatively adsorbed on the CZ surface. The predicted rate determining steps are surface reactions of methane precursors on the interface between the active Rh metal and the CZ support. Chen et al. [181] investigated nickel loaded ceria rich solid solution catalysts for dry methane reformation for hydrogen production. The catalytic activity of the solid solution was enhanced by nickel loading. Yue et al. [182] reported the methane combustion over Pd loaded CZ solid solution supported with alumina. Best catalytic activity in the combustion was mainly due to the high thermal resistance and oxygen storage capacity of the system with well dispersed Pd particles on the catalyst surface. Mei et al. [183] reported the partial oxidation of methane over nickel loaded CZ supported alumina. Like the above catalyst, this nickel loaded CZA catalyst provided the higher activity. Pavlova et al. [184] reported the partial oxidation of methane over alumina supported CZ solid solution and reported a lower methane conversion towards hydrogen and carbon oxides. The reason provided is that the catalytic activity depends on the catalyst composition and pre-treatment. Sadykov et al. [185] investigated the methane oxidation over calcium and fluoride modified Pt/CZ solid solutions. They concluded that the lattice oxygen present in the catalyst reacts with methane and forms CO and H_2 at 500°C and the oxygen capacity is balanced by the re-oxidation of the reduced systems with the liberation of syngas. Laosiripojana and Assabumrungrat [186] reported that $Ni/CeZrO_2$ system enhances the steam reformation of methane for the production of hydrogen and found that the catalyst provided high resistance to carbonaceous deposit, due to the redox properties of CZ solid solution.

Ceria-zirconia solid solution is used in the catalytic combustion of methane for the H_2 production [187-189]. Later, it was discovered that doping with Mn or Cu on the solid solution will enhance their activity to a better extent [190]. Bozo et al. [189] reported total methane oxidation over the Pt and Pd supported CZ solid solution. They established that, doping of Pd and Pt strongly increases the catalytic activity at low reaction temperatures and proposed that the oxidation of methane takes place at the CZ-metal interface based on the reaction of dissociated methane and the lattice oxygen of the catalyst. Silva et al. [191] studied the partial oxidation of methane over Pt loaded CZ solid solution supported with alumina, containing 0-40% CZ solid solution. They prepared homogeneous solid solution catalysts containing 10 and 20 wt % of CZ and then ceria rich and zirconia rich phases were detected from the 30% CZ system. But in the case of 40% catalyst, zirconia phase were monitored. For the methane oxidation, 10 and 20% catalysts showed deactivation resistance compared with the other catalysts, which may be due to the high OSC and reducibility of the solid solution. This is responsible for the replacement of the carbon deposited on the surface of the Pt metal units. Zhang et al. [192] reported the methane oxidation reaction over AuOx loaded CZ solid solution containing yttria. Best catalytic activity is due to the well dispersed gold nanoparticles on the catalyst surface. This catalyst showed the superior activity among the Au loaded other supports due to the reducibility power. They suggested that the best activity may be due to the stabilization of gold nanoparticles and the oxide species at the gold-support interface and the oxygen vacancies of the redox CZY support. Sim et al. [193] investigated hydrogen production through the redox cycles using the methane and water over tungsten oxide loaded ceria-zirconia. They proved that the ceria-zirconia mixed oxide has the capacity to stabilise the tungsten oxides. As a result of this, the formation of carbon oxides can be minimised and high hydrogen selectivity was observed. Yuan et al. [194] investigated the autothermal reformation of methane over Rh/MgO promoted homogeneous CZ solid solution for hydrogen production. All components of the catalyst together enhanced the OSC and showed a better performance in this reaction. Because of the high selectivity to hydrogen gas, it should be noted that the catalyst has excellent activity in water gas shift reaction. The catalyst provided high coke resistance during the continuous run without any deactivation.

Chen et al. [195] reported the hydrogen generation by heterogeneous catalytic decomposition of HI, which is produced by the sulphur-iodine thermochemical cycle [196]. They observed that Pt loaded CZ solid solution shows much more efficiency than blank run. The decomposition efficiency was found to be temperature dependent. HI decomposition was 7% at 300°C, a maximum of 22% at 550°C and good catalytic results were also observed at other temperatures. The catalytic features like thermal stability and OSC enhanced by Pt loading on CZ solid solution are the main reasons for the increased conversion of HI to hydrogen at the mentioned higher temperatures. Iojoiu et al. [197] investigated the hydrogen production from biomass derived oil over Pt and Rh loaded CZ catalysts or deposited on cordierite monoliths by the pyrolysis method. They proved that the successive thermal and catalytic cracking of bio-oil could be effectively used for the hydrogen production over the prepared CZ solid solution system, which controls the coke deposition and its removal remedy. They also found that the rate of hydrogen production of both catalysts were of almost similar in the initial stage and then a small deactivation was noticed for the Pd containing sample compared to the Rh sample which is mainly related to the oxygen stored in the Pd-CZ catalyst. Continuous hydrogen production was observed for the monolith catalyst compared with the powder samples. Rioche et al. [198] has reported the bio oil derived compound's steam reformation over the noble metals Pt, Pd and Rh promoted CZ solid solution and alumina for the production of hydrogen. They noted that the noble metal loaded ceria zirconia solid solution showed much higher activity in the hydrogen generation compared with the alumina catalysts, which may be due to the improved structural and textural properties of the CZ solid solution obtained by the noble metal loading and the enhancement of reducibility and high oxygen storage and release capacity.

Zheng et al. [199] investigated the steam reformation of bio oil derived acetic acid for the hydrogen production over various nickel loaded CZ catalysts. Among them, 12% nickel loaded ceria rich CZ solid solution provided the better catalytic activity at 650°C with a hydrogen selectivity of 83.4% with negligible amount of methane. The catalysts have the capacity to resist deactivation for 25 hours for continuous run. They suggested that the active component, Nickel present in the sample enhanced the breaking of the carbon-carbon bond and carbon-hydrogen bond for the production of hydrogen and for the well dispersion of the nickel. Ceria played a major role in the CZ solid solution. Gal and Abanades [200] reported the production of hydrogen through the water splitting method using the solar thermochemical route over CZ solid solution prepared by the co-precipitation method. They studied the effect of the zirconium content from10% to 50% on the redox nature of the CZ system and reported that increase in the Zr content does not increase the hydrogen yield. With 25% Zr solid solution, they got 334 and 298 mmol H_2 and with 50% Zr system, they got 468 and 266 mmol H_2 per gram of the catalyst at 1050°C during the consecutive runs. From this, it is clear that reasonable Zr contents may prefer H_2 production without affecting the activity of the catalyst for the consecutive runs.

Mastalir et al. [201] investigated the methanol steam reformation for the production of syngas over copper loaded CZ mixed oxide and reported that the catalysts with high % of Cu provided high stability and low yield of CO during the continuous run of reaction. The kinetic model predicted by them suggested that the steam reformation of methanol is accompanied by the water gas shift reaction and the decomposition of methanol. High methanol conversion was observed for the steam reformation of methanol over the Cu/CZ catalyst at lower temperatures (250°C-270°C), under these conditions low CO was noticed. Xue et al. [202] investigated the hydrogen production from the methanol decomposition reaction over Pd supported CZ solid solution promoted with lanthana. The high catalytic activity of the present catalyst was mainly due to the enhanced textural properties of the CZ solid solution attained by lanthana doping, which promote the re-oxidation of the palladium in its zero and partially positive oxidation states. Over the present catalyst, complete methanol conversion was noticed at 340°C, below this temperature lower conversions were observed for the methanol.

Zhao et al. [203] also reported the same reaction with the additional support lanthana in the Pd solid solution. They reported that using Pd doped solid solution, 100% methanol conversion was obtained over the catalyst. Surface acidity of the catalyst and the chemical state of palladium affected the methanol decomposition. Liu et al. [204] investigated various Pd loaded CZ solid solutions for methanol decomposition. They obtained syngas with 96% selectivity and 51.2% conversion for co-precipitated one and 17.2% for the impregnated one with the catalyst composition of 17wt % Pd loaded CZ solid solution (Ce: Zr molar ratio 4:1). The catalysts showed activity at lower reaction temperatures. Vargas et al. [205, 206] reported the hydrogen production by bio-ethanol steam reformation using cobalt loaded fluorite type solid solution prepared by the propionate polymerisation in solution method and this catalyst showed greater ethanol conversion and high hydrogen selectivity. It is observed that the Ni/CZ catalyses the hydrogen production by the steam reformation of ethanol [207, 208]. Biswas and Kunzru [207] investigated the ethanol steam reformation for hydrogen production over nickel loaded CZ solid solution. Among the various catalyst systems used in the reaction, 30% nickel loaded ceria rich solid solution presented superior catalytic activity with 100% ethanol conversion and high selectivity towards the hydrogen gas with lower contaminants of carbon oxides and methane at a reaction temperature of 600°C. Zirconia rich composition of CZ systems showed very lower activity in the reaction. The highest activity of the efficient nickel loaded system may be due to the presence of high lattice oxygen, contributing to the high OSC of the ceria rich solid solutions and also due to the availability of huge amount of reduced nickel on the catalyst surface. The ethanol conversion found to be increased with the nickel amount and the catalyst provided good resistance to deactivation for the continuous run for a day.

3.3.1. *Applications in water gas shift reaction (WGS)*

Water gas shift reaction may produce hydrogen and CO_2 for a wide variety of industrial applications. It involves the chemical reaction of CO with water vapour and almost shows unification with steam reformation of methane for the hydrogen production. WGS involves oxidation of CO to CO_2 and it may involve the corresponding reduction of the catalyst support. So many catalysts are found to be used for the purpose. But much great attention was caught for the CZ solid solution. Low and high temperature water gas shift reactions are reported based on the thermodynamic limitations [209-211]. Hilaire et al., Qi et al. and Jacobs et al. [212-214] reported the water gas shift reactions using solid solution. Ricote et al. [215] investigated the low temperature water gas shift reaction over Pt loaded ceria zirconia mixed oxides. The low reaction temperature was mainly due to the binary CZ mixed oxide formed by the incorporation of zirconia into the ceria lattice and accumulation of zirconia in the ceria lattice reduced the temperature for surface reduction of ceria. They explained that there are two formate species, which are involved in the reaction, one is on the surface of cerium ion and other with the zirconium ion and reported that, by increasing the zirconia insertion to the ceria lattice, the rate of formate decomposition is promoted, which is the responsible factor for the better activity of the catalyst for the water gas shift reaction compared with other catalyst systems, Pt/ceria or Pt/zirconia. Vindigni et al. [216] investigated the water gas shift reaction over Au loaded pure ceria and its zirconia modified form and reported that the best catalytic activity was shown by Au loaded CZ solid solution with the homogeneous composition rather than the pure ceria and the ceria rich CZ solid solution at the lower reaction temperatures. The best catalytic activity of the homogeneous system is due to the enhanced acidity of the ceria-zirconia along with the presence of well dispersed Au nanoparticles and Au clusters on the CZ support surface.

Halabi et al. [217] investigated the methane steam reformation over Rh /CZ catalyst and established that at lower reaction temperatures, more CO_2 was detected in the gaseous product, which is mainly due to the catalytic activity in water gas shift reaction. As the temperature increases, the steam to carbon ratio decreases and the water gas shift reaction gets a decline. They explained that methane and the steam are dissociatively adsorbed on the rhodium site and the CZ support respectively in the catalyst during the course of the reaction and indicated the high stability of the catalyst, which prevents the coke deposition. Large selectivity of the catalyst was observed for the water gas shift reaction. Carbon oxides formation reactions on the catalyst surface determine the rate of this reaction.

Watanabe et al. [218] reported the water gas shift reaction using Ni-Fe loaded CZ solid solution prepared through the hard template route. The formation of Ni-Fe alloy loaded CZ solid solution is confirmed by various analytical methods. The catalyst showed more activity and selectivity towards the water gas shift reaction. A mechanism for the reaction over the catalyst was proposed. A site having an affinity towards an O-species (Fe site) in the metallic portion will accept an oxygen, provided by the CZ solution support, with the simultaneous adsorption of CO molecule by the other site which shows a strong affinity towards the CO, (Ni site) for the generation of adsorbed specious along with the oxygen vacant support. Then the CO oxidation takes place with CO_2 generation with the liberation of free active sites. Then the oxidation of metallic ion site takes place by water and hydrogen liberation and finally the oxygen vacant support will receive oxygen from the active iron site and the catalyst is regenerated. Liu et al. [219] used the Pt loaded CZ solid solution for WGS reaction and noted high conversion and selectivity for the reaction, due to the high surface area of the support and strong interaction between the platinum and the support. Again Liu et al. [220] studied the Pt loaded ceria rich solid solution prepared via the micro emulsion method for WGS reaction. They reported that there is no methanation during the reaction, but the activity of the catalyst was lower in pure syngas and higher in sour syngas because it has a capacity to resist the accumulation of H_2S and sulphates on the support, providing high catalytic activity in sour syngas.

A large number of studies are done in the WGS reaction based on the gold loaded CZ solid solution. Idakiev et al. and Burch [221, 222] reported that solid solution act as a good support in the water gas shift reaction in gold catalysis. The main attraction of the support is the highly stabilised structure and the high OSC in the surface and bulk of the solid solution. Fonseca et al. [223] reported very active Au/CZ solid solution for the low temperature water gas shift reaction. Boaro et al. [224] reported the same reaction with both Pt and gold loaded solid solution and compared the result with metal loaded zirconia. They concluded that even though the gold is shown better activity than Pt loaded solid solution, the effect of support is very low impact in accordance with the observation that the redox properties played a subordinate role and the metal support interface played a superior role in the WGS reaction. But in comparison with zirconia, Boaro et al. reported that ceria only modifies the redox property and Zr is the good support for gold in WGS catalysis. Deshpande et al. [225] also have the same report that the metal (Pd and Pt) doped solid solution has lower activity at higher temperatures in comparison with the zirconia catalyst systems for water–gas shift reaction. All the systems exhibited good CO conversion with equivalent formation of H_2. Pd substitution was inferior as compared to Pt substituted catalysts, but Pd showed the higher activity than Pt ion. Mechanism is that the noble metal causes the generation of oxide ion vacancy in the solid solution and then the adsorption of CO on the noble metal ion surface. Here the OSC plays a secondary role in the reaction in agreement with Boaro et al. [224]. Cu loaded CZ solid solutions were found to have a great application in water gas shift reaction [226], due to the formation of ceria-copper oxide solid solution in addition to the achievement of high catalytic performance of the CZ solid solution on the metal doping.

3.4. ***Application in oxygen gas sensors***

Among various gas sensors, major studies have been concentrated on the exhaust gas oxygen sensors. A large number of studies are now on-going in oxygen sensors especially in the resistive oxygen sensors which use ceria based materials as oxygen partial pressure measurement material. The temperature-independent resistive oxygen sensor has been now invented using an oxygen partial pressure measurement material and a temperature compensating material. Manorama et al. [227] found that the Pt loaded ceria prepared by the hydrazine hydrate method showed maximum sensitivity in the temperature range of 807°C-1507°C in oxygen sensing process and reported that Pt incorporation reduced the response time and provided an improved gas sensing power. This type of sensor eliminates the temperature dependence of the ceria. CZ solid solutions are now used as stable solid state reference material in low cost oxygen sensors because of their high OSC and thermal stability. Rajabbeigi et al. [228] fabricated an oxygen sensor using CZ solid solution with 25% zirconia as the solid state reference. The sensor has yttria stabilised zirconia as the electrolyte and Pt coated CZ solid solution as the electrode. The developed sensor displayed a sharp variation in the voltage ranges from 350mV to −80 mV. On contrary to the conventional sensors, which shows voltage variation from 1000 mV to 100mV, the present oxygen sensor fulfilled the concept of fast response and low cost. The enhanced applicability of the sensor is mainly due to the high thermal resistance and oxygen storage capacity of the solid state reference, i.e. CZ solid solution. Again Rajabbeigi et al. [229] fabricated the oxygen sensor by employing the ternary mixed oxide of CeO_2-ZrO_2-TiO_2 as the solid state reference. The sensor has the yttria stabilised zirconia as electrolyte and Pt coated CZT reference layers as the electrode. The sensor produced a wide hysteresis in the lean region at a temperature of 400°C, but a finer hysteresis was noticed at higher temperatures and showed a voltage variation from +300 mV in gas rich region to -250mV in the lean region, on contrary to the conventional oxygen sensors. Applicability of this sensor is mainly due to the proper thermo-mechanical correlation between electrolyte and the ternary solid solution reference.

Izu et al. [230] fabricated the resistive oxygen sensor based on the thick film made from zirconia doped ceria powders with particle size of 100 nm. With increase in the amount of zirconia (10%), the resistance of the thick film decreased and its resistance was found to be 1/10 that of the thick film without zirconia. They indicated that, for 10 and 20 mol % zirconia containing CZ thick films, the response time was 16 and 9 minutes respectively at an operating temperature of 800°C. The prepared CZ nanopowders presented large oxygen partial pressure dependence and hence good oxygen sensitivity in a wide range of pressures from 10-17 to 105 Pa. Chen and Chang [231] fabricated the resistive oxygen sensor using ceria-zirconia nanopowders as the solid state reference. It showed high temperature independence and was successfully applied to the temperature range of 650°C-850°C. For the fabrication of this oxygen sensor, they used CZ solid solution films with 10% and 5% zirconia as the oxygen partial pressure measurement material and temperature compensating material respectively. The active response of the resistive oxygen sensor with the solid solution demonstrated its high sensitivity and stability. The output voltage of the fabricated oxygen sensor was found to be not correlated with the operating temperatures; and reported that this feature is the predominant factor for the development good oxygen sensors. They reported the conductive nature of CZ solution in accordance with the partial pressures of oxygen with respect to the temperature, which is the factor responsible for the well performed CZ solid solution temperature independent oxygen sensors. The sensor can be considered as a promising nominee for a temperature independent oxygen sensor due to its outstanding sensitivity and stability. As per many reports, the oxygen sensors with 10% zirconia doped ceria as solid state reference can distinct the fuel rich and fuel lean conditions in an equilibrium state. Izu et al. [232] fabricated the resistive oxygen sensor based on the Pt doped CZ solid solution. By the optimization of Pt content present in the CZ sample, the sensor can differentiate very effectively in the fuel rich and lean conditions in the non-equilibrium state. They also observed that the response time duration was upgraded by the Pt catalyst. Again Izu et al. [233] investigated the use of resistive oxygen sensor using ceria rich CZ solid solution as a sensor material for lean-burn engines. The temperature dependence of the TCM should be equivalent to the sensor material. For the fabrication process, ceria-zirconia and ceria-yttria solid solutions were utilised and the output voltage measurements showed that the sensor is independent of temperature from 500-800°C. Ghom et al. [234] reported that the mesoporous CZ solid solution has the potential to act as a good oxygen sensor.

CONCLUSION

Based on the heterogeneous catalytic applications of metal loaded CZ solid solutions, vast studies have been on-going in its synthesis and characterisation. The introduction of metals into CZ solid solution stimulates the thermal stability, oxygen storage capacity and redox properties of the solid solution. Ceria zirconia solid solution showed its prominent activity in the simultaneous elimination of nitrogen oxides, carbon monoxides and hydrocarbons. Special role is observed in the detoxification of chlorinated hydrocarbons and also in the oxidation of soot particles from the diesel exhaust engines, so that the CZ solid solution and its metal loaded form may act as eco-friendly catalysts. Application of metal doped CZ in an energy point of view is focused on the hydrogen production technologies. It presented active role in the steam reforming and thermal cracking of natural gas for the hydrogen production. Water gas shift reaction for syngas production was also catalysed by these systems. However its activity for the water splitting reaction and oxygen sensors caught much special attention in recent years.

Acknowledgements
This project is financed by Universiti Kebangsaan Malaysia under grant AP-2012-008. The authors would like to thank the university administration for the financial support.

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