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Hydrogen production from simple alkanes and oxygenated hydrocarbons over ceria–zirconia supported catalysts: Review

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Abstract

The use of ceria–zirconia based catalysts in hydrogen production from simple alkanes and oxygenated hydrocarbons for the processes of steam reforming (SR), autothermal reforming ('ATR'), catalytic partial oxidation ('CPO'), and dry reforming ('DR') are reviewed in this paper. Along with preparation methods, the effects of operating conditions like molar steam to carbon ratio, oxygen to carbon ratio, and temperature on the performance of hydrogen production from methane, acetic acid, ethanol, and glycerol were examined. SR and ATR of these feedstocks over ceria–zirconia supports have been widely investigated. In comparison the utilization of these supports in the CPO and DR processes has been investigated mainly for methane as compared to oxygenated hydrocarbons. Ce-rich supports were reported to be effective in hydrogen from SR and ATR of ethanol and glycerol and in SMR in the 'low' temperature range (500–600 °C), whereas zirconium-rich supports exhibited higher catalytic activity in the 'high' temperature range (700–800 °C). In the case of DR, Ce-rich supports were effective at high temperature.
The methods of preparation of the supports/catalyst are shown to affect the surface area (catalyst/support), crystallite size of (active metal/support), reducibility and dispersion of the active metal, thus affecting performance of the catalyst.

Abbreviations: ACCP, ammonium carbonate co-precipitation; AMCP, ammonia co-precipitation; AHCP, ammonium hydroxide co-precipitation; ATR, autothermal reforming; ATRE, autothermal reforming of ethanol; ATRM, autothermal reforming of methane; C, catalyst; CP, co-precipitation; CPOM, catalytic partial oxidation of methane; CPOE, catalytic partial oxidation of ethanol; DR, dry reforming; DRM, dry reforming of methane; HRTEM, high resolution transmission electron microscopy; IMP, impregnation; ME, micro-emulsion; MS, molten salt; MSSG, molten salt sol gel; OSC, oxygen storage capacity; PD, precipitation digestion; PFA, palm fatty acids; PFAD, palm fatty acid distillate; PH, potassium hydroxide; PHCP, potassium hydroxide co-precipitation; PHPP, potassium hydroxide precipitation; RME, reverse micro-emulsion; S, support; SA, surfactant assisted; SACP, surfactant assisted co-precipitation; SG, sol gel; SIMP, sequential impregnated; SCCP, sodium carbonate coprecipitation; SHCP, sodium hydroxide co-precipitation; SMR, steam methane reforming; SR, steam reforming; SRA, steam reforming of acetic acid; SRE, steam reforming of ethanol; SRG, steam reforming of glycerol; TEM, transmission electron microscopy; UC, urea combustion; UH, urea hydrolysis

Keywords: Hydrogen; Ceria–zirconia; Steam reforming; Autothermal reforming; Partial oxidation; Dry reforming

1 Introduction

Ceria based materials have attracted serious attention for utilization in automotive exhaust catalyst, ceramics, fuel cell technologies, gas sensors, solid state electrolytes, and ceramic biomaterials [1–6]. Ceria is an effective material in promoting reactions of catalytic carbon dioxide activation, carbon monoxide oxidation, carbon monoxide/nitrous oxide removal, and catalytic combustion of methane [7,8]. Ceria plays an important role in most important commercial catalytic processes like fluid catalytic cracking (FCC) [1], diesel soot oxidation [9], and oxidation of volatile organic compounds [10]. One of the crucial property of a ceria based material is its oxygen storage capacity (OSC) by means of redox shift between Ce3+ and Ce4+ under oxidizing and reduction environments [11]. Ceria exhibits superior catalytic activity for water gas shift reaction [12]. It is also well known to promote metal activity and dispersion, resulting in investigations of various catalytic formulations for a wide range of reactions.
The OSC of ceria helps to reduce the formation of carbon, over ceria supported catalyst during hydrogen production, methane oxidation, methane decomposition, and ethylene dehydrogenation reactions. Further, Ni supported ceria based catalysts have exhibited self-decoking capability by promoting carbon gasification reaction by supplementing oxygen species from the latice oxygen. [13].
Hydrogen production from gaseous hydrocarbons like methane, ethane, propylene, butane, and liquefied petroleum gas (LPG) over ceria supported catalysts have been reported by Xu et al. [14], Pino et al. [15], Wang and Gorte [16], and Laosiripojana and Assabumrungrat [17]. Ceria supported catalysts were also reported to convert poisonous methanethiol (CH3SH) to hydrogen-rich gas via the solid–gas reaction between ceria and methanethiol [18]. In the presence of steam, formation of Ce(SO4)2 was reported to occur during the steam reforming (SR) reaction leading to high methanethiol reforming activity. Likewise hydrogen production from liquid hydrocarbons like methanol, ethanol, glycerol and propanol were investigated by several authors [19–21]. However ceria lacks thermal stability and is known to sinter at temperature above 800 °C [22], leading to catalyst deactivation [23,24]. At high temperature the specific surface area of ceria decreases drastically which in turn affects the crucial redox properties and OSC of the material [25]. The OSC of pure ceria is unsatisfactory for practical applications. Ceria consists of eight oxygen cations coordinated at a corner of cube, each anion being tetrahedrally coordinated by four cations. This makes ceria's structure more stable and prevents the conversion of Ce4+ to Ce3+ under reducing conditions. Metal decoration has been observed for metal catalysts supported on reducible oxides [26]. Deterioration of catalytic activity is also caused by decreases in metal surface area on metal supported catalysts [27].

Hydrogen production from gases like methane using endothermic SR process is carried out at high temperature i.e. 800 °C or higher, resulting in decrease in surface area by ~30% with operation for 10 h [23]. Similarly the increase in the temperature of the ceria supported catalyst as a result of exothermic nature of partial oxidation reaction results in sintering of the ceria and affecting activity of the catalyst.

Improvement of the thermal properties of ceria and retention of active surface area at high temperature is thus necessary to exploit the redox property of ceria for hydrogen production applications via high temperature processes like catalytic partial oxidation ('CPO'). Substitution of ceria with metal/metal oxide into the ceria lattice forms composite oxides. Ceria can easily form solid solutions with elements belonging to the transition-metal series. Ionic mobility is modified by replacement of cerium ions by different cations of varying size and/or charge resulting in the formation of a defective fluorite structured solid solution. The crystal structure of Ce0.75Zr0.25O2 obtained by zirconium doped ceria is shown in Fig. 1.

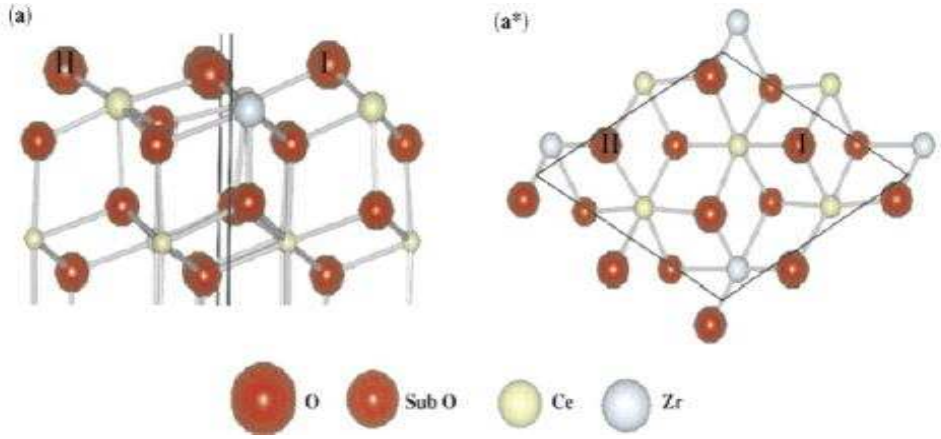

Fig. 1 Crystal structure of Ce0.75Zr0.25O2. In (a) shows the side view and (a□) represents the top view of the Ce0.75Zr0.25O2. The labels 'I' and 'II' represent two types of surface oxygen ions; the big red, small red, yellow, and blue shows surface oxygen, subsurface oxygen, Ce, and Zr, respectively [28]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Fig. 2 shows a high resolution transmission electron microscopy (HRTEM) image of Ce0.75Zr0.25O2 prepared using the decomposition and co-precipitation method [29].

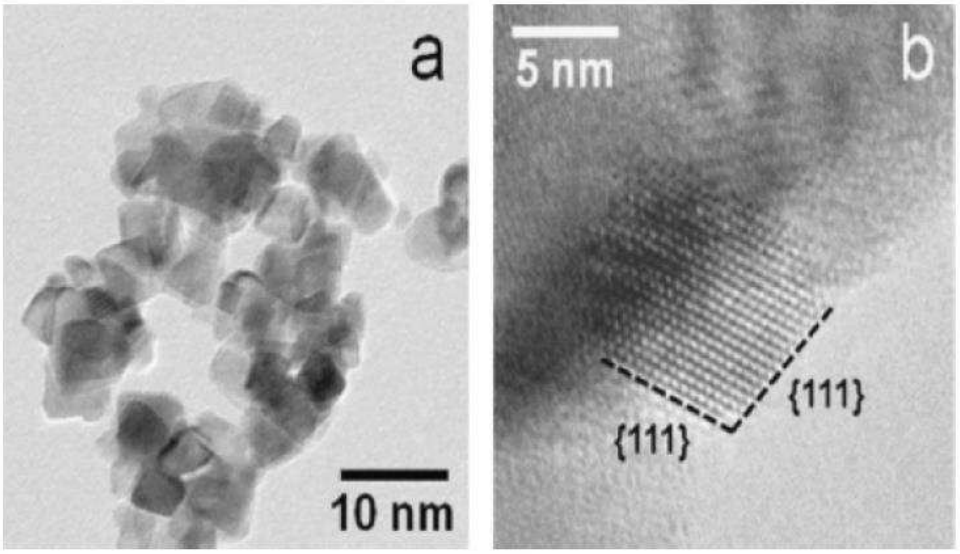

Fig. 2 HRTEM image of $Ce_{0.75}Zr_{0.25}O_2$ prepared using the decomposition and co-precipitation method calcined at 500 °C [29].

This modification of ceria lattice confers properties like resistance to sintering and high catalytic activity [30–32]. Incorporation of Zr increases the specific surface area, OSC, redox property, thermal stability and catalytic activity of ceria [33–35]. It also affects the dispersion of metals supported on the Zr doped ceria. A transmission electron microscopy (TEM) image of dispersed Rh and Pt particles of fresh RhPt supported on 17.5 wt% CeO2–ZrO2 are shown in Fig. 3 [36].

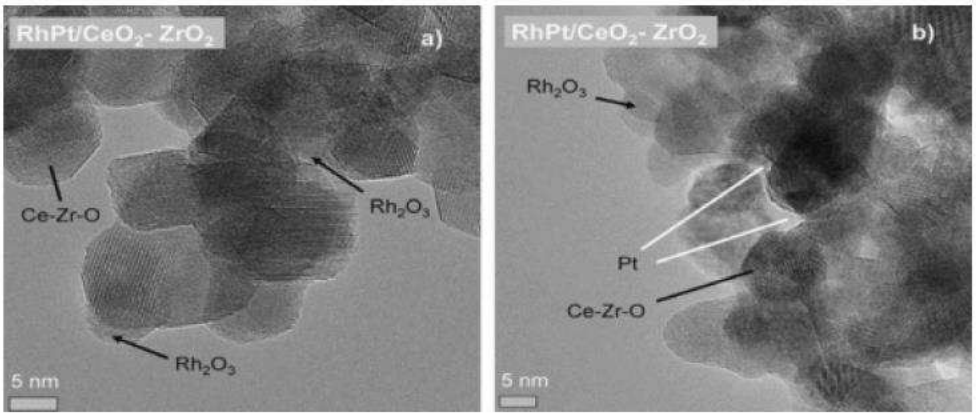

Fig. 3 TEM images of dispersed Rh and Pt particles of fresh RhPt supported on 17.5 wt% CeO_2–ZrO_2 catalyst [36].

Tables 1 and 2 show the effects of the preparation method on the surface area, OSC, and metallic dispersion of Ce–ZrO2 supported metal catalysts utilized in hydrogen production processes. Further addition of Zr to Ce also helps in mitigating the formation of carbon during various hydrogen production processes [25]. Table 3 lists the amount of carbon deposited on various metals supported Ce–ZrO2 catalysts prepared by varied methods, utilized in hydrogen production processes.

Table 1 Effect of preparation methods on the physicochemical properties of $Ce–ZrO_2$ supported catalysts utilized in hydrogen production.

Authors	Investigation	Support	Active metals	Method of preparation	Surface area m^2/g	Support size (nm)	Active metal size (nm)
Roh et al. [47]	SMR	$Ce_{0.8}Zr_{0.2}O_2$	15 wt% Ni	15 wt% Ni	168[b]	5.2	
Roh et al. [62]	SRE	$Ce_{0.2}Zr_{0.8}O_2$	2 wt% Rh	aq-AMCP	98[b]		
Lin et al. [58]	SRE	$Ce_{0.75}Zr_{0.25}O_2$	10 wt% Co	SHCP	92.5[b]	4.5	–
Jun et al. [119]	DRM	$Ce_{0.8}Zr_{0.2}O_2$	15 wt% Ni	AMCP	92	5.9	12.5
Kusakabe et al. [45]	SMR	$Ce_{0.5}Zr_{0.5}O_2$	10 wt% Ni	U H	81.1[a]	–	–
Roh et al. [61]	SRE	$Ce_{0.8}Zr_{0.2}O_2$	2 wt% Rh	PHPD	61	–	
Dong et al. [49]	SMR	$Ce_{0.2}Zr_{0.8}O_2$	15 wt% NI	M S	55[a]	–	112
Roh et al. [60]	SRE	$Ce_{0.13}Zr_{0.87}O_2$	1 w% Rh	Commercial	44[a]	–	
					44[b]		
Shotipruk et al. [56]	SR of PEAD	$Ce_{0.75}Zr_{0.25}O_2$	5 wt% Ni	SA-aq-AMCP	46.5[a]	–	–
Laosiripojana et al. [24]	SMR	$Ce_{0.75}Zr_{0.25}O_2$	5 wt% Ni	SA-aq-AMCP	41.5[a]	–	–
					19.5[b]	–	–
			5 wt% Rh			–	–
Laosiripojana et al. [55]	SR of PEAD				40.9[b]		–
Roh et al. [48]	SMR	$Ce_{0.2}Zr_{0.8}O_2$	15wt %Ni	SG	44[b]		12.7
Roh et al. [46]	SMR	$Ce_{0.2}Zr_{0.8}O_2$	15wt %Ni	S G	40[b]		
Biswas and Kunzru [19]	SRE	$Ce_{0.74}Zr_{0.26}O_2$	30 wt% Ni	aq-AMCP	22.8[a]	12.5	17.3
					19.5[b]		
Dave and Pant [21]	SRG	CeO_2/10 w% ZrO_2	15 w% Ni	IMP	22[b]	–	–
Hu et al. [67]	SRA	5 w% CeO_2–ZrO_2	5 wt% Ni	AHCP	20.6[b]	–	–
Zheng et al. [66]	SRA	7.5 w% CeO_2–ZrO_2	12 wt% Ni	IMP	14.61[b]	–	–

[a] Support.

[b] Catalyst.

Table 2 Effect of preparation methods on OSC and metal dispersion of metal supported on $Ce–ZrO_2$ catalysts, utilized in hydrogen production.

Author	Investigation	Method of preparation	Catalyst/support	Reported OSC value/hydrogen uptake (μmol/gcat)	Metallic dispersion (%)
Siliva et al. [85]	POM	IMP	0.5 wt%Pt–$Ce_{0.75}Zr_{0.25}O_2$–Al_2O_3	246[b]	100
			1.0 wt%Pt–$Ce_{0.5}Zr_{0.5}O_2$–Al_2O_3	245[b]	77
			1.5wt %Pt–$Ce_{0.25}Zr_{0.75}O_2$–Al_2O_3	242[b]	57
			1.5 w% Pt/40% $Ce_{0.5}Zr_{0.5}O_2$/Al_2O_3	783[b]	68
Siliva et al. [96]			1.5 w% Pt/20% $Ce_{0.5}Zr_{0.5}O_2$/Al_2O_3	483[b]	64
			1.5 w% Pt/10% $Ce_{0.5}Zr_{0.5}O_2$/Al_2O_3	291[b]	58
			1.5 w% Pt/30% $Ce_{0.5}Zr_{0.5}O_2$/Al_2O_3	588[b]	57
Silva et al. [95]	POM	Co-IMP	1.5 wt%Ni–$Ce_{0.25}Zr_{0.75}O_2$–Al_2O_3	115[b]	54
			1.5 wt%Ni–$Ce_{0.5}Zr_{0.5}O_2$–Al_2O_3	565[b]	49

Silva et al. [94]			1.5 wt%Pt–$Ce_{0.75}Zr_{0.25}O_2$–Al_2O_3	215[b]	47
			1.5 wt%Pt–$Ce_{0.75}Zr_{0.25}O_2$–Al_2O_3-pp	215[b]	42
Roh et al. [62]	SRE	aq-AMCP	2 wt%-Rh–$Ce_{0.8}Zr_{0.2}O_2$	–	46.3
Roh et al. [60]		IMP	1 wt%-Rh–$Ce_{0.87}Zr_{0.13}O_2$		
Boullosa-Eiras et al. [99]	POM	IMP	0.5 wt%Ni–$Ce_{0.5}Zr_{0.5}O_2$–Al_2O_3	–	41
			0.5 wt%Ni–$Ce_{0.25}Zr_{0.75}O_2$–Al_2O_3	–	38
Ruiz et al. [72]	ATRM	AHCP	1.5 wt%Pt–$Ce_{0.75}Zr_{0.25}O_2$–800	626[a]	22
			1.5 wt%Pt–$Ce_{0.75}Zr_{0.25}O_2$–900	726[a]	11
Roh et al. [47]	Combined methane reforming	PHCP	5 w %-Ni–$Ce_{0.8}Zr_{0.2}O_2$	–	7.96
Roh et al. [48]	SMR				6.60
Roh et al. [50]	SMR	IMP	15 wt%Ni–$Ce_{0.2}$ $Zr_{0.8}O_2$–Al_2O	42.85[b]	4.99
			12 wt%Ni–$Ce_{0.2}$ $Zr_{0.8}O_2$–Al_2O_3	32.80[b]	4.96
			6 wt%Ni–$Ce_{0.2}$ $Zr_{0.8}O_2$–Al_2O_3	13.50[b]	4.70
			3 wt%**Ni**–$Ce_{0.2}$ $Zr_{0.8}O_2$–Al_2O_3	5.38[b]	3.53
Laosiripojana et al. [55]	SR of PFAD	SA-aq-AMCP	5 wt%-Rh–$Ce_{0.75}Zr_{0.25}O_2$	–	4.62
Kumar et al. [123]	DRM	SA-aq-AMCP	5 wt%-Ni–$Ce_{0.60}Zr_{0.4}O_2$	–	4.30
Dong et al. [49]	SMR	SG	10 w %-Ni–$Ce_{0.2}Zr_{0.8}O_2$	7.32	1.05
				7.32[b]	0.86
			15 w %-Ni–$Ce_{0.2}Zr_{0.8}O_2$	11.5[b]	0.74
				93.8[b]	0.41
			20 wt%-Ni–$Ce_{0.2}Zr_{0.8}O_2$	0.799[b]	0.48
			3 wt%-Ni–$Ce_{0.2}Zr_{0.8}O_2$		
Roh et al. [68]	SMR	SG	3 wt%-Ni–$Ce_{0.2}Zr_{0.8}O_2$	228.8[a]	0.86
			15 wt%-Ni–$Ce_{0.2}Zr_{0.8}O_2$	214.9[a]	
Roh et al. [46]			15 wt%-Ni–$Ce_{0.2}Zr_{0.8}O_2$	9.39[a]	
Lisboa et al. [73]	ATRM	AHCP	10 wt%Ni–$Ce_{0.75}Zr_{0.25}O_2$	551[a]	0.68
Biswas and Kunzru [19]	SRE	aq-AMCP	20 wt%Ni–$Ce_{0.74}$ $Zr_{0.26}O_2$	7.14[b]	0.42
			30 wt%Ni–$Ce_{0.74}Zr_{0.26}O$	7.60[b]	0.30
			30 wt%Ni–$Ce_{0.74}Zr_{0.26}O_2$	2.03[b]	0.24

			40 wt%Ni–$Ce_{0.74}Zr_{0.26}O_2$	6.27[b]	0.19
Chen et al. [115]	DRM	AMCP	0.5 wt%Ru–$Ce_{0.75}Zr_{0.25}O_2$	0.7[c]	–
			1 wt%Ru–$Ce_{0.75}Zr_{0.25}O_2$	1.1[c]	
			1.5 wt%Ru–$Ce_{0.75}Zr_{0.25}O_2$	8.9[c]	
			3 wt%Ru–$Ce_{0.75}Zr_{0.25}O_2$	14.5[c]	
Damyanova et al. [114]	DRM	IMP	1 wt%-Pt–1 wt%-CeO_2–ZrO_2	0.51	–
			1 wt%-Pt–3 wt%-CeO_2–ZrO_2	0.57	
			1 wt%-Pt–6 wt%-CeO_2–ZrO_2	0.62	
			1 wt%-Pt–12 wt%-CeO_2–ZrO_2	1.25	
Quingwei et al. [100]	POM	PP	10 wt%Ni–$Ce_{0.7}Zr_{0.3}O_2$–Al_2O_3	–	1.16
		Mixing-PP	10 wt%Ni–$Ce_{0.7}Zr_{0.3}O_2$–Al_2O_3		0.75
		Mechanically mixing	10 wt%Ni–$Ce_{0.7}Zr_{0.7}O_2$–Al_2O_3		0.46
Shotipruk et al. [56]	SR of PFAD	SA-aq-AMCP	5 wt% Ni–$Ce_{0.75}Zr_{0.25}O_2$	5313[b]	–
Sukonket et al. [124]	DRM	SA-aq-AMCP	$Ce_{0.64}Zr_{0.4}O_2$-1.25	1093	–
			$Ce_{0.6}Zr_{0.4}O_2$-0.8	1031	
			$Ce_{0.6}Zr_{0.4}O_2$-0.5	93	

[a] Support.

[b] Catalyst.

Table 3 Effect of preparation methods on reducibility of metal supported on Ce–ZrO_2 catalysts utilized in hydrogen production.

Authors	Investigation	Preparation method	Catalyst/support	Metal reducibility (%)
Biswas and Kunzru [19]	SRE	aq-AMCP	10% Ni/$Ce_{0.74}Zr_{0.26}O_2$	97.3
Abreu et al. [51]	SMR	ACCP	5 wt%Ni–$Ce_{0.6}Zr_{0.4}O_2$–Al_2O_3	96.4
Roh et al. [50]	SMR	IMP	15 wt%Ni–$Ce_{0.2}Zr_{0.8}O_2$–Al_2O_3	92.3
Laosiripojana et al. [55]	SR of PFAD	aq-AMCP	5 wt%Rh–$Ce_{0.75}Zr_{0.25}O_2$	92
Roh et al. [48]	Combined methane	aq-AMCP	15 wt%Ni–$Ce_{0.8}Zr_{0.2}O_2$	53.7
Roh et al. [47]	Reforming SMR	aq-AMCP	15 wt%Ni–$Ce_{0.8}Zr_{0.2}O_2$	40.8

Table 4 Effect of preparation methods on carbon production on metal supported Ce–ZrO_2 catalysts utilized in hydrogen production.

Authors	Investigation	Preparation method	Catalyst/support	C
Jun et al. [119]	DRM	CP	15 wt%Ni–$Ce_{0.8}Zr_{0.2}O_2$	<0.0001 g_C g cat^{-1}
Abreu et al. [51]	SMR	ACCP	5 wt%Ni–$Ce_{0.6}Zr_{0.4}O_2$–Al_2O_3	0.34 mmol h^{-1}[a]
Vagia and Lemonidou [65]	SRA	IMP	5 wt% Ni–$Ce_{0.86}Zr_{0.16}O_2$	1.5 wt% of catalyst[b]
			0.5 wt% Rh–$Ce_{0.86}Zr_{0.16}O_2$	0.5 wt% of catalyst[b]
Laosiripojana et al. [108]	PO of PFAD	aq-AMCP	5 wt%Ni–$Ce_{0.75}Zr_{0.25}O_2$	3.9 mmol C $gcat^{-1}$
Kamonsuangkasem et al. [80]	ATRG	IMP	5% wt% Ni/8%CeO_2–ZrO_2–Al_2O_3	4.4 mmolC $gcat^{-1}\,h^{-1}$-S/C=1[c]
				4.3 mmolC $gcat^{-1}\,h^{-1}$-S/C=2[c]
				4.2 mmolC $gcat^{-1}\,h^{-1}$-S/C=3[c]
Shotipruk et al. [56]	**SR of PFAD**	**aq-AMCP**	**5 wt%Ni–$Ce_{0.75}Zr_{0.25}O_2$**	**5.1 mmol $gcat^{-1}$[d]**
	ATR of PFAD			**3.9 mmol $gcat^{-1}$[d]**
Laosiripojana et al. [55]	**SR of PFAD**	**aq-AMCP**	**5 wt%Rh–$Ce_{0.75}Zr_{0.25}O_2$**	**10 mmol C $gcat^{-1}$[e]**
	ATR of PFAD			**3.5 mmol C $gcat^{-1}$[e]**
Qingwei et al. [100]	**POM**	**CP with mixing**	**10 wt%Ni/$Ce_{0.7}Zr_{0.3}O_2$/γ-Al_2O_3**	**19.2**
		CP		**14.7**
		Mechanical mixing		**7.1**

[a] Catalyst was evaluated for 350 min at 750 °C at S/C of 2.

[b] The performance of the catalyst was evaluated at 900 °C at S/C of 3 for 10 h. The ATR evaluation was performed using O_2/C of 1.

[c] The performance of the catalyst was evaluated at 800 °C at S/C of 3 for 48 h. The PO and ATR experiments were performed using O_2/C of 1.

[d] The catalyst performance was evaluated at O_2/C of 0.15 at 550 °C.

[e] The catalyst was evaluated for 3 h at 750 °C at S/C of 3.

The inclusion of Zr4+ or Hf4+ into ceria lattice facilitated an increase in the formation of smaller particle sizes. In addition, incorporation of Zr also increases the oxygen mobility in the ceria lattice and the process of vacancy formation, thus increasing the reducibility of the material [33,37,38]. This extends ceria reduction deep into the bulk of the material, rather than confining to the surface [34,39]. Addition of Zr increases the interactions between the support and the metal. During the reductive treatment, transfer of Ce4+ to the support surface takes place, resulting in the formation of ceria-rich phase on the surface while the phenomenon is reversed when atmosphere was switched to an oxidative atmosphere [40]. Fig. 4 shows a migration model of Ce4+ and oxygen vacancies during the reductive/oxidative treatments of ceria–zirconia mixed oxide [40]. An oxidation treatment was shown to increase the reducibility of the oxide. In case of Pt supported on ceria–zirconia mixed oxide, Pt sites and the Ce Pt located at the interface interact, and transfer of electrons from the metal oxide to the noble metal occurs. This results in the lowering of effective activation energy, necessary for the formation of oxygen vacancies, resulting in high oxidation activity [40,41]. Fig. 5 shows a shell–core structure of Pt crystallites and the decoration/encapsulation by ceria–zirconia support during the reductive/oxidative treatments [40]. The percentage of reducible Ce4+ is known to increases with Zr/Ce ratio. The effect of preparation methods on the reducibility of metal supported Ce–ZrO2 catalyst used in hydrogen production processes is shown in Table 3.

This review examines the application of ceria based material in hydrogen production from simple alkanes and oxygenated hydrocarbons using various processes. Methods of preparation, operating conditions and performance of the catalyst in terms of hydrogen yield, selectivity, molar composition and fuel conversion are also investigated.

2 Hydrogen production

Several processes to produce hydrogen-rich gas for fuel cell applications are being employed today. Hydrogen can be produced using catalytic steam reforming (‘SR’), catalytic partial oxidation (‘CPO’), autothermal reforming (‘ATR’),and CO2 reforming of methane, which is also known as dry reforming (‘DR’). SR is the most common process used to produce hydrogen in industry. Hydrocarbon fuel is reacted with steam at high temperature around 800 °C. The reaction is performed in tubular packed bed reactors called reformers on Ni based catalyst in Raschig rings using a molar H2O/CH4 ratio typically between 2 and 5, but most often around 2.5. Alkali metals are used in the catalyst to accelerate carbon removal. Excess steam is used to prevent carbon formation. SR reaction is strongly endothermic, and reactor designs are typically limited by heat transfer, rather than by reaction kinetics [42]. The general SR reaction is represented by R-1 and R-2 explains steam methane reforming (‘SMR’).

$$\text{Steam reforming (SR)}: \; C_nH_mO_k + (n-k)H_2O \overset{\Delta H>0}{\rightleftharpoons} nCO + \left(\frac{m}{2}+n-k\right)H_2 \quad \text{R1}$$

$$\text{Steam methane reforming}\left(\text{SMR}\right): \; CH_4 + H_2O \overset{\Delta H_o=206.2\,\text{kJ/mol}}{\rightleftharpoons} CO + 3H_2 \quad \text{R2}$$

Partial oxidation ('PO') is exothermic reaction. If higher oxygen is fed, combustion reaction also occurs, resulting in the formation of carbon dioxide and steam rather than carbon monoxide and hydrogen. In addition PO is kinetically faster than SR and requires smaller reactors and exhibits higher productivity [43]. A major drawback of PO is the formation of flammable and explosive environments. Hot spots can develop affecting the life of the catalyst [44]. Reaction R-3 represents a generic reaction for the PO of oxygenated hydrocarbons. The PO of methane is given by reaction R-4.

$$\text{Partial oxidation (PO)}: \ C_nH_mO_k + \frac{(n-k)}{2}O_2 \xrightarrow{\Delta H_0 < 0} nCO + \frac{m}{2}H_2 \qquad \text{R3}$$

$$\text{Partial oxidation (PO)}: \ CH_4 + \frac{1}{2}O_2 \xrightarrow{\Delta H = -36.02\ \text{kJ/mol}} CO + 2H_2 \qquad \text{R4}$$

Autothermal reforming (ATR) is a combination of SR and CPO reactions. The method uses exothermic heat of the oxidation reactions to provide the heat required by the endothermic reforming reaction in a single unit to produce hydrogen-rich gas. The method is useful for small scale hydrogen production because of faster start up, small size, higher efficiency, fuel flexibility and hydrogen purity. Reactions R-1 and R-3 take place in ATR along with the complete oxidation reaction R-5, which includes the reactions R-6 to R-7.

$$\text{Oxidation (Ox)}: \ C_nH_mO_k + \left(n + \tfrac{m}{4} - 0.5k\right)O_2 \rightarrow nCO_2 + \tfrac{m}{2}H_2O \qquad \text{R5}$$

$$\text{Oxidation } (CO_x): \ CO + \frac{1}{2}O_2 \xrightarrow{-283.6\ \text{kJ/mol}} CO_2 \qquad \text{R6}$$

$$\text{Oxidation } (O_x): \ H_2 + \frac{1}{2}O_2 \xrightarrow{-241.6\ \text{kJ/mol}} H_2O \qquad \text{R7}$$

In addition to the above hydrogen production methods, CO2-reforming of methane, also termed 'dry reforming' (DR) has recently received some interest as reforming method because of its carbon dioxide recycling potential. In this method the fuel is reacted with carbon dioxide to form syngas. In case of dry reforming synthesis gas having H2/CO ratio of 1 is produced making it suitable for F-T synthesis. Reaction R-8 shows the general case where a hydrocarbon undergoes dry-reforming, with R-9 representing the dry reforming of methane.

$$\text{Dry reforming (DR)}: \ C_nH_m + nCO_2 \overset{\Delta H_R > 0}{\rightleftharpoons} 2nCO + \frac{m}{2}H_2 \qquad \text{R8}$$

$$\text{Dry reforming (DR)}: \ CH_4 + CO_2 \overset{\Delta H_0 = 247.3\ \text{kJ/mol}}{\rightleftharpoons} 2CO + 2H_2 \qquad \text{R9}$$

DRM is the most endothermic of the reforming reactions due to the large negative enthalpy of CO2. Side reactions like water gas shift (R-10), methanation (R-11), carbon formation (R-12), carbon monoxide disproportionation (Boudouard reaction

(R-13)), gasification reaction (R-14), and oxidation reactions (R15–16) can take place on the catalyst surface , affecting the performance of the above mentioned processes.

$$\text{Water gas shift (WGS)}: \; n(CO + H_2O \overset{\Delta H_o = -41\ kJ/mol}{\rightleftharpoons} CO_2 + H_2)$$

$$\text{Methanation (MTH)}: \; n(CO + 3H_2 \overset{\Delta H_o = -213.8\ kJ/mol}{\rightleftharpoons} CH_4 + H_2O)$$

$$\text{Decomposition (D)}: \; (C_mH_nO_k \rightarrow (n-k)\,C + \frac{m}{2}H_2 + kCO$$

$$\text{Boudouard (Boud)} (2CO \overset{\Delta H_o = -171.5\ kJ/mol}{\rightleftharpoons} CO_2 + C)$$

$$\text{Coke gasification (GS)}\; C + H_2O \overset{\Delta H_o = 139\ kJ/mol}{\rightleftharpoons} CO + H_2$$

$$\text{Coke oxidation (CO)}\; C + \frac{1}{2}O_2 \overset{\Delta H_o = -110.5\ kJ/mol}{\rightarrow} CO$$

$$\text{Coke oxidation (CO)}\; C + O_2 \overset{\Delta H_o = -395.6\ kJ/mol}{\rightarrow} CO_2$$

(R10 to R16)

2.1 Steam reforming

Ce–ZrO2 supported catalysts have been widely investigated in hydrogen production via SR, CPO, ATR, and WGS reactions. The following section describes the use of various ceria–zirconia supported catalysts in SR of alkanes and oxygenated hydrocarbons.

2.1.1 Steam methane reforming (SMR)

Kusakabe et al. [45] examined the effect of noble metals supported on Ce–ZrO2 material prepared by urea hydrolysis (‘UH’), for SMR in the temperature range 500–600 °C using a molar steam to carbon ratio (‘S/C’) of 2. Over Pt and Rh supported catalyst the conversion increased with loading from 1 to 3 wt% but further loading lowered conversion. Contradictorily in case of Ru based catalyst conversion improved with loading, in the entire range examined (1 to 5 wt %). The authors reported that a cubic structure based mix oxide (Ce0.5Zr0.5O2) exhibited higher activity in comparison to (Ce0.75Zr0.25O2) supports, contrary to Laosiripojana et al. [24], who found that Ce0.75Zr0.25O2 exhibited higher activity than other phases of Ce–ZrO2 supports in SMR. Carbon monoxide selectivity was higher over noble metals in comparison to Ni based catalyst possibly as a result of dehydrogenation of methane. SMR over 5 wt%-Ni/Ce–ZrO2 at 900 °C was examined by Laosiripojana and Assabumrungrat [23] using S/C of 3. The support was prepared by UH of metal salts by varying the molar ratio of Ce to Zr (‘Ce/Zr’) from 1 to 3. Ce0.75Zr0.25O2 exhibited the best performance among the catalysts examined. The support prepared using this method had lower surface area as compared to the supports prepared using the ammonia co-precipitation (‘AMCP’) method [24].The authors examined the effect of surfactant addition in the support

preparation method which involved AMCP of cerium and zirconium nitrate salts. Addition of surfactant considerably increased the support surface area.

In spite of higher catalytic activity slight deactivation due to the sintering of material was reported. The addition of the surfactant was also shown to affect the dispersion of the Ni[24]. At odds with these results Roh et al. [46] reported similar results over 15 wt% Ni supported on Ce0.2Zr0.8O2 prepared by the molten salt method ('MS') at 750 °C using S/C of 3.

Roh et al. [47] examined low temperature SMR over Ni supported on potassium hydroxide precipitation ('PHPP') Ce–ZrO2 supports. The effect of Ce/Zr on the performance of the catalyst was evaluated using 10 wt% Ni loading at 600 °C and S/C of 1, with Ce0.8Zr0.2O2 exhibiting the best performance. The higher activity of the catalyst was attributed to higher thermal stability, higher redox capability of Ce–ZrO2, smaller Ni crystallite size resulting in higher carbon resistance, cubic phase of the support improving the reducibility and thus helping in the reduction of metal sintering.

Roh et al. [48] compared the impregnation ('IMP') and co-precipitation ('CP') methods for preparation of 15 wt% Ni supported Ce0.8Zr0.2O2 catalyst in SMR with small amount of carbon dioxide. The activity of Ce–ZrO2 based catalysts using S/C ratio of 1 and CH4/CO2 of 0.5 was examined between 700 and 800 °C. The Ni Ce ZrO2 catalyst prepared by the CP method was found more effective as compared to the conventional IMP catalyst. Highest activity as well as stability of the CP catalyst was attributed to nano-sized crystallite of both Ce0.8Zr0.2O2 and NiO resulting in the formation of intimate contact between Ni and the support, improved Ni dispersion, and finally enhanced reducibility and oxygen transfer during the reaction. Smaller crystallite size of support and NiO was reported over the CP catalyst in comparison to the impregnated ones. Ni dispersion and surface area were quite high over the CP catalyst compared as to the impregnated ones.

Effect of Ni loading on the performance of sol gel ('SG') prepared Ce0.8Zr0.2O2 supported catalyst in SMR at 750 °C and S/C of 3 was examined by Dong et al. [49]. Ni surface area and hydrogen uptake were reported to increase with loading from 3% to 20% and upon further increase in loading they decreased, which was attributed to sintering of Ni particles. The activity of the catalyst was related to the dispersion of the catalyst and Ni surface area. Higher loading catalyst exhibited higher average crystallite sizes, promoting carbon formation. The high activity of the catalyst was mainly as a result of good balance between two kinds of active sites, i.e. one for the activation of methane and the other for that of steam or oxygen.

In comparison to Ni impregnated Ce0.8Zr0.2O2 catalyst, Ni/Ce0.2Zr0.8O2/θ-Al2O3 catalyst prepared by the IMP method exhibited better performance in SMR at 800 °C with S/C of 1 [50]. The high stability of the catalyst was mainly ascribed to the beneficial precoating effect of Ce–ZrO2 which resulted in the formation of stable NiOx species, a strong interaction between Ni and the support, an abundance of mobile oxygen species, resulting in high carbon resistance. Authors reported that methane conversion increased with Ni loading from 3 to 12 wt% but further increases reduced conversion. Abreu et al. [51] reported dissimilar results over 5 wt% Ni supported on Ce0.2Zr0.8O2–γ-Al2O3 catalyst in SMR, prepared using the ammonium hydroxide coprecipitation ('AHCP') method at S/C of 2.1 and 750 °C. Although the Zr-rich catalyst initially exhibited higher conversion, it underwent severe deactivation with time on stream. The catalyst with higher Ce content was reported to help in the reduction of Ni species, which otherwise resulted in increased methane decomposition to form carbon. But the presence of Ce favoured the activation of steam resulting in carbon gasification, leading to a stable catalytic formulation.

2.1.2 Steam reforming of methanol (SRMe)

Like methane, Ce–ZrO2 has been investigated widely in ethanol ('SRE') [19,52,53], glycerol ('SRG') [21], bio-oils [54], and complex oxygenated hydrocarbons like palm oil fatty acid ('PFAD') [55,56]. But Ce–ZrO2 has not been investigated widely in SR of methanol ('SRMe') [20,57], the motive of the investigations was to utilize this support to produce high purity hydrogen and prevent the formation carbon monoxide using oxygen vacancies from the support. The use of 8 wt% Cu supported on CeO2/ZrO2 at 250 °C was investigated by Oguchi et al. [57]. During the SR reaction CuO was reduced to metallic Cu, which, although it exhibited high activity for SRMe, it suffered sintering of crystallites. Addition of Zr leads to the formation of Cu2O rather than CuO.
Presence of Cu2O was shown to affect the durability of the catalyst by being less reducible to metallic Cu, during the SR reaction. Addition of Zr maintained the formation of Cu2O under the reducing environment in SRMe conditions, by providing an oxygen source (OH) and maintaining the oxidation state of Cu. Further addition of Zr led to increase in Cu aggregation, and helped in the formation of smaller Cu2O species than metallic Cu.
A 3 wt% Au supported Ce–ZrO2 catalyst for SRMe was investigated by Pojanavaraphan et al. [20] in the temperature range of 200 to 500 °C using S/C of 2. The evaluation of different support compositions revealed Ce0.75Zr0.25O2 to exhibit the best performance. The formulations with higher Zr content had a negative effect on the performance of the catalyst by increasing Au particle size. Two different support preparation methods i.e. sodium carbonate co-precipitation ('SCCP') and UH followed by IMP of Au salts were evaluated. Both the methods of preparation exhibited similar performance. The increase in pH up to 7 had a positive effect on the performance of CP catalyst. Addition of Cu to Au exhibited similar performance to Cu based catalyst.
Addition of Cu was shown to preserve the small alloy size and result in the formation of Au–Cu alloy thereby significantly promoting SRMe.

2.1.3 Steam reforming of ethanol (SRE)

SRE over Ni/Ce–ZrO2 prepared by AMCP and incipient wetness IMP technique was investigated by Biswas and Kunzru [19] at S/C of 4 between 400 and 650 °C. A 30 wt% Ni supported on cubic phased Ce0.74Zr0.26O2 support exhibited the best catalytic activity. Like Roh et al. [48] who reported the high activity of Ni/Ce0.8Zr0.2O2 in SMR, they attributed high activity to the extent of reduction of Ni in the catalyst. Higher Ni loading up to a certain amount resulted in increase in reduced Ni enhancing the activity of the catalyst. High OSC capacity of the catalyst increased the availability of surface oxygen on the material, enhancing the WGS reaction, resulting in high activity. On the other hand Ye et al. [53] reported that a 20 wt% Ni catalyst supported on cubic Ce0.5Zr0.5O2 exhibited high activity for SRE with S/C of 1.5 between 350 and 600 °C.

Unlike Ni supported catalyst, Co supported on cubic Ce0.75Zr0.25O2 catalyst prepared by the IMP method exhibited higher activity in comparison to the supports prepared by the CP method, in SRE Lin et al. [58]. The activity of the catalyst was examined over 10 wt%-Co/Ce0.75Zr0.25O2 with S/C of 6.5 at 450 °C. Under SR conditions a formation of unidentified active phase resulting from reaction between the partially reduced Co and Ce–ZrO2 catalyst was reported to exhibit superior catalytic activity. The authors attributed the high activity of the catalyst to the reduction behavior of the catalyst like Biswas and Kunzru [19] and

Roh et al. [48]. A weaker contact between the active metal and support was seen, which was partially reduced during reduction of the catalyst.
Maia et al. [59] examined the use of 10 wt% Co/Ce0.8Zr0.2O2 prepared by ethylene glycol and the citric acid polymerization method, in SRE. The activity of the catalyst was measured using S/C of 1.5 between 400 and 600 °C. High activity of the catalyst was found to be temperature dependent as a result of doping of Ce with Zr which yielded enhanced oxygen vacancies and redox capacity of the support to promote the oxidation of carbon monoxide. Higher activity of Co for WGS reaction was one of the factors responsible for increasing the activity of the catalyst at lower temperatures.
Roh et al. [60] described a 2 wt% Rh on cubic phased Ce0.13Zr0.87O2 prepared by the IMP method exhibiting high catalytic activity in SRE. Similar to Ni based catalysts, strong interaction between Rh and the support play an important part in enhancing oxygen transfer efficiency during ethanol SR reactions. The catalyst promoted dehydrogenation or C–C cleavage of ethanol rather than dehydration, thus exhibiting high catalytic activity. In a different evaluation the increase in Zr in Rh supported on Ce–ZrO2 decreased the activity of the catalyst in SRE [61]. Roh et al. [61] examined the effect of Ce/Zr ratio on performance of Rh based catalyst in SRE using S/C of 4 at 450 °C. They reported that the 2 wt% Rh supported on Ce0.2Zr0.8O2 most severely deactivated among all the formulations studied, as a result of increased ethylene formation. Addition of 0.5% potassium ('PH') had a beneficial effect on catalyst stability, while higher potassium content (about 5%) lowered the catalytic activity. A Ce0.8Zr0.2O2 support was the best formulation as a result of higher OSC, and strong interaction between Rh and Ce0.8Zr0.2O2 had a positive effect on the performance of the catalyst reflected in an increased oxygen transfer efficiency [62]. The deactivation behavior of this formulation was studied by Platon et al. [44]. Addition of acetone and ethylene to the feed caused deactivation of 2 wt% Rh supported on Ce0.8Zr0.2O2 prepared by the AMCP method, in SRE at 350 °C and S/C of 4. But the catalyst activity was recovered by addition of small amount of oxygen which regenerated the deactivated catalyst.
A different reason for deactivation of 1.5 wt% Pt/Ce0.75Zr0.25 O2 in SRE was reported by de Lima et al. [63]. SRE was performed by the authors using S/C of 1.5 at 500 °C. Catalyst deactivation was attributed to acetate or carbonate species observed on the surface of the catalyst. The O2 defects on ceria promoted activation of H2O to OH groups. The OH groups reacted with carbon monoxide to produce formate molecule. Pt assisted the dehydrogenation of the formate molecule resulting in carbonate formation. Like Ye et al. [53], Birot et al. [64] reported high activity over 1 wt% Rh supported on commercial Ce0.5Zr0.5O2 at 600 °C with S/C of 2. The catalyst had high selectivity to methane. Carbon monoxide and carbon dioxide hydrogenation over the catalyst was examined by the authors with CO/H2 and CO2/H2 of 4 between 400 and 600 °C. The catalyst catalyzed carbon monoxide and carbon dioxide methanation reactions.

2.1.4 Steam reforming of oxygenated hydrocarbons

Similarly to Roh et al. [60], Vagia and Lemonidou [65] reported that 0.5 wt% Rh supported Ce0.86Zr0.16O2 catalyst prepared by the IMP method exhibited high catalytic activity in steam reforming of acetic acid ('SRA'), used as a model component of biooil.
The activity was attributed to low affinity towards carbon formation and high oxygen mobility of Ce–ZrO2 facilitating surface oxidation reactions to the metal interface leaving the surface of the catalyst clean. Yan et al. [54] gave accounts of similar results during SR of bio oil over sequential impregnated ('SIMP') of Ni and Ce over ZrO2 prepared using the CP method to obtain a Ni/CeO2–ZrO2 catalyst.

Increase in temperature and Ni loading affected the catalytic activity. While increase in Ce loading along with S/C increased activity up to certain value, on further increase of S/C it decreased the activity. The catalyst exhibited higher catalytic activity compared to a commercial catalyst. The best performance was reported over 12 and 7.5 wt% Ni and Ce loading respectively, with water/bio oil ratio of 4.9 at 800 °C exhibiting highest hydrogen yield. Similarly Zheng et al. [66] examined the use of 12 wt% Ni supported on Ce–ZrO2 catalyst obtained using the CP method, in SRA at 650 °C with S/C of 3. An optimum Ce content of 7.5 wt% was reported, similar to Yan et al. [54], but the optimum results were obtained at 650 °C in comparison to 800 °C. Higher temperatures i.e. 700 °C were reported to promote reverse WGS over the catalyst. At 600 °C and lower S/C of 1.5, Hu et al. [67], reported that 12 wt% Ni supported on Ce–ZrO2 prepared using the CP method, with Ce content of 5 wt% deactivated as result of formation of acetone and carbon monoxide. Polymerization of acetone and carbon monoxide disproportionation reactions were reported responsible for catalyst deactivation. Higher temperature helped in preventing carbon formation from carbon monoxide disproportionation due to OSC of the material, but acetone polymerization was unaffected with rise in temperature.

Ni supported on cubic Ce0.75Zr0.25O2 prepared by the surfactant assisted co-precipitation ('SACP') method was reported to exhibit high activity in SR of complex oxygenated hydrocarbons like palm fatty acid distilled ('PFAD') by Shotipruk et al. [56]. The catalyst performance was evaluated at 900 °C with S/C of 3. The catalyst provided the highest SR reactivity along with greatest carbon deposition resistance as a result of high OSC of this material. Also, comparison of model components of PFAD showed increase in the formation of ethylene with increase in degree of unsaturation from palmitic to linoleic acid, which meant increase in carbon content. But the degree of unsaturation also corresponded to a lower selectivity to hydrogen. High activity over 5 wt% Rh/Ce0.75Zr0.25O2 at slightly lower temperature i.e. 800 °C at S/C of 3 over a support prepared by the same SACP method was reported by Laosiripojana et al. [55]. As compared to Ni based catalyst, the Rh ones exhibited higher carbon formation i.e.
10 mmol/gcat compared to 5.1 mmol/g cat at respective conditions. Higher selectivity to ethylene was observed over the Rh based catalyst resulting in higher carbon formation. At 900 °C, the Rh based catalyst exhibited higher activity as compared to the Ni based catalyst.

Simultaneous IMP was adopted by Dave and Pant [21] in SR of glycerol (SRG), in comparison to CP, POL, SG, and UH, IMP methods investigated by other authors. High activity was reported over 10 wt% Ni loading supported on 10 wt% zirconia promoted ceria. Addition of zirconia improved the crystallinity of the ceria which in turn improved the metallic dispersion there by affecting the activity of the catalyst. Further addition of zirconia resulted in a very small amount of methane being produced thus increasing the selectivity towards hydrogen.

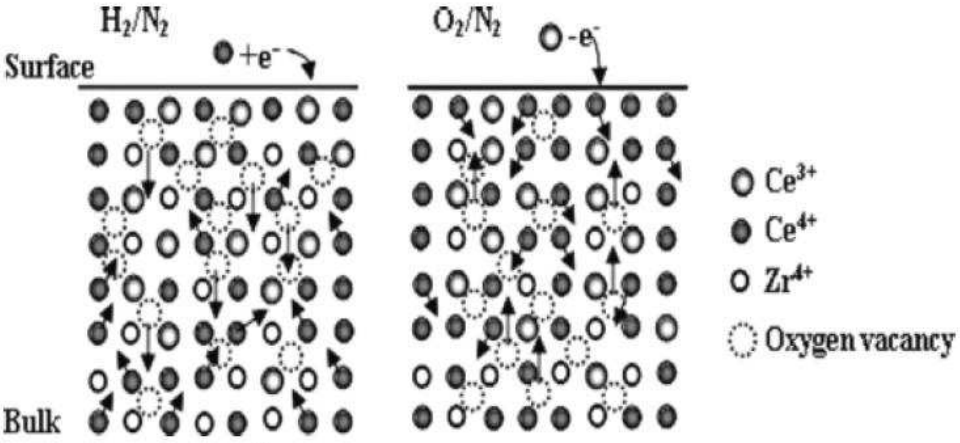

Fig. 4 A migration model of Ce^{4+} and oxygen vacancies during the reductive/oxidative treatment of ceria–zirconia mix oxide [40].

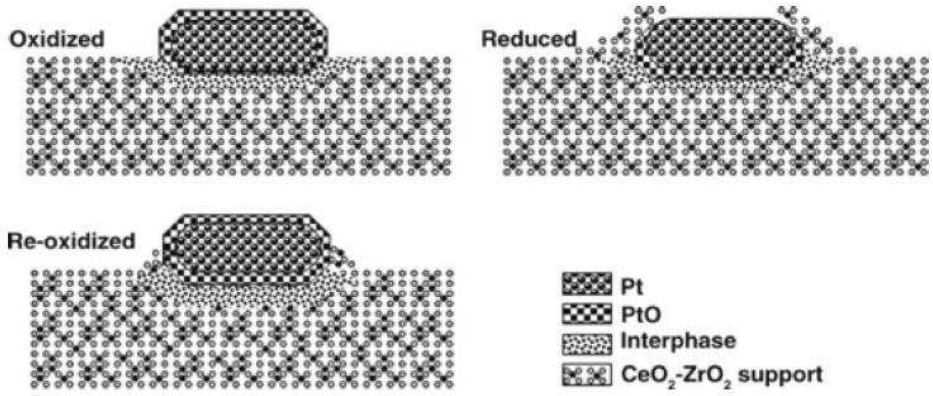

Fig. 5 A shell–core structure of Pt crystallites and the decoration/encapsulation by ceria–zirconia support during the reductive/oxidative treatments [40].

Table 5 Performance of $Ce–ZrO_2$ supported metal catalysts in terms of hydrogen production obtained in SR of simple alkane and oxygenated hydrocarbons.

Author	Investigation	Conditions			Definition		Reported values			
		Catalyst	S/C	Temp (C)	Yield Y (%)	Selectivity S (%)	Y (%)	S (%)	Conversion (%)	Molar comp (%
Vagia and Lemonidou [65]	SRA	0.5 wt% Rh–$Ce_{0.15}Zr_{0.85}O_2$	3	750	23		90[a]	–	100	
		5 wt% Ni–$Ce_{0.15}Zr_{0.85}O_2$					85		100	
Zheng et al. [66]	SRA	12%-Ni/7.5 wt% CeO_2–ZrO_2	3	650		23		~85	100	–
Shotipruk et al. [56]	SR of PFAD	5 wt% Ni–$Ce_{075}Zr_{0.25}O_2$	3	900	–	–	–	70[b]	100	–
Roh et al.[62]	SRE	1 wt% Rh–$Ce_{0.13}Zr_{0.87}O_2$	4	450	17	30	3.7	72	100	–
Roh et al. [50]	SMR	12 wt%Ni–$Ce_{0.2}Zr_{0.8}O_2$–Al_2O_3	1	800	–	–	85		83	
Roh et al. [47]	SMR	15 wt% Ni–$Ce_{0.8}$ $Zr_{0.2}O_2$	4	600	–	–	60.8[c]	–	59.5[c]	
Roh et al. [60]	SRE	2 wt% Rh–$Ce_{0.2}Zr_{0.8}O_2$	4	450	–		4.08		40	
Laosiripojana et al. [55]	SR of PFAD	5 wt% Rh–$Ce_{0.75}Zr_{0.25}O_2$	3	800	19	–	56.7	–	~100[b]	–
Biswas and Kunzru [19]	SRE	30 wt% Ni–$Ce_{0.74}Zr_{0.26}O_2$	4	650	17	–	5.7	–	99.7	73.92
Kusakabe et al. [45]	SMR	3 wt%Rh–$Ce_{0.15}Zr_{0.85}O_2$	3	800	–	–	–	–	98.6	–
		3 wt% Pt–$Ce_{0.15}Zr_{0.85}O_2$							84.9	
		3 wt%Ru–$Ce_{0.15}Zr_{0.85}O_2$							77.3	
		10 wt% Ni–$Ce_{0.15}Zr_{0.85}O_2$							66.6	
Roh et al.[46]	SMR	10 wt% Ni–$Ce_{0.2}$ $Zr_{0.8}O_2$	3	750	22		115		~97[d]	62[d]
Pojanavaraphan et al. [20]	SMRe	3 wt% Au–$Ce_{0.75}Zr_{0.25}O_2$	2	400	–	–	–	–	>95	60
Dave and Pant. [21]	SRG	15 wt%-CeO_2/10 wt% -ZrO_2	15.33[e]	700	18	26	3.9	62.53	90.3[f]	–
Dong et al. [49]	SMR	30 wt% Ni -$Ce_{0.2}Zr_{0.8}O_2$	3	750	–	–	–	>75	60.9	–
Abreu et al. [51]	SMR	5 wt%Ni–$Ce_{0.8}$ $Zr_{0.2}O_2$–Al_2O_3	2.1	750	–	–	–		60	3.5[g]
		5 wt%Ni–$Ce_{0.2}$ $Zr_{0.8}O_2$–Al_2O_3							>70	2.4 [h]
Laosiripojana et al. [24]	SMR	5 wt% Ni–$Ce_{0.75}Zr_{0.25}O_2$ (LSA)[h]	3	900	–	–	–	–	~50	–
		5 wt% Ni–$Ce_{0.75}Zr_{0.25}O_2$ (HSA)[i]							>70	
Lin et al. [58]	SRE	10 wt% Co–$Ce_{0.75}Zr_{0.25}O_2$	6.5	450	21		80[j]			75[j]
Yan et al. [54]	SRA	12%-Ni/7.5 wt% CeO_2–ZrO_2	4.9	800	23		69.7			>55

In table 5:
a In durability test at 650 °C activity decreased slightly in first 4 h, but remained fairly constant for next 11 h.
b The values were reported over a period of 50 h.
c The values were reported over 5 h of evaluations.
d The values were recorded over 200 min.
e Calculated based on 10 wt% glycerol solution.
f Conversion of glycerol into gaseous products.
g Highest molar composition was observed in first 50 min of evaluation decreasing slightly after that and remaining fairly constant for 350 min.
h Molar composition increased in first 50 min of the evaluation, remaining constant up till 250 min and decreasing further on up till the end of evaluation.
i LSA and HSA represent low and high surface area.
j The values were measured at 0.005 mol/h flow rate.

2.2 Autothermal reforming

Like SR, Ce–ZrO2 supported catalysts have been investigated in ATR of hydrocarbons like methane, ethanol, glycerol, and bio-oils [68–70]. The following section describes the investigations of ceria–zirconia supported catalyst in ATR of simple alkane and oxygenated hydrocarbons.

2.2.1 Autothermal reforming of methane (ATRM)

The effect of catalyst preparation method over 0.1 wt% Rh/Ce0.5Zr0.5O2 was investigated in ATRM by Cao et al. [71] using S/C of 2 and molar oxygen gas to carbon ratio (O2/C) of 1.5 at 850 °C. The authors prepared catalysts using various methods like reverse micro-emulsion (‘RME’), CP, urea combustion (‘UC’), and SG. The findings suggested that reducibility and OSC of Ce0.5Zr0.5O2 solid solution was significantly affected by the crystal structure. The best activity was reported for the catalyst prepared with ME, among the methods examined. The superior performance of the catalyst was attributed to a single cubic phase as opposed to tetragonal and mixed phases observed from the other methods.
In contrast, Ruiz et al. [72] reported decreasing activity in ATRM over 1.5 wt% Pt supported on Ce0.5Zr0.5O2 obtained using the AHCP method. The catalysts were tested using S/C of 0.2 and O2/C of 0.5 at 800 °C. Deactivation occurred due to low Pt dispersion, resulting in low metal-support interfacial area. The lower OSC value along with larger Pt particle size reduced the carbon removal effectiveness of the catalyst, resulting in higher carbon deposition. Cubic phased Ce0.75Zr0.25O2 showed the best performance among the formulations examined as a result of higher OSC, which helped in continuous removal of carbonaceous deposits from the active sites at the metal-support interfacial perimeter. Addition of small amount of carbon dioxide was useful in increasing methane conversion over Ce0.75Zr0.25O2 based catalyst, but also affected catalyst stability after 24 h of evaluation.
Roh et al. [46] reported high activity in SMR of Ni/Ce0.2Zr0.8O2 prepared by the SG method. The same catalyst exhibited higher activity under ATR conditions in comparison to SR. ATRM was performed using S/C of 3 over 15 wt% Ni supported on Ce0.2Zr0.8O2 prepared using the MS method. Dong et al. [49] and Roh et al. [68] found that mobiles oxygen species formed in the catalyst via a redox cycle enhanced decoking activity. Formations of composite layers of material were thought to be the reason for high activity. The composite was made of three different layers with top layer consisting of free Ni species followed by second layer of strongly interacted Ni and Ce ZrO2 forming Ce Zr Ox, finally the last layer of Ce ZrO2 support. Fig. 6 shows a schematic of the Ce–ZrO2 catalyst structure

reported by Roh et al. [68]. The participation of the lattice oxygen was supplemented by the presence of O2 molecules.

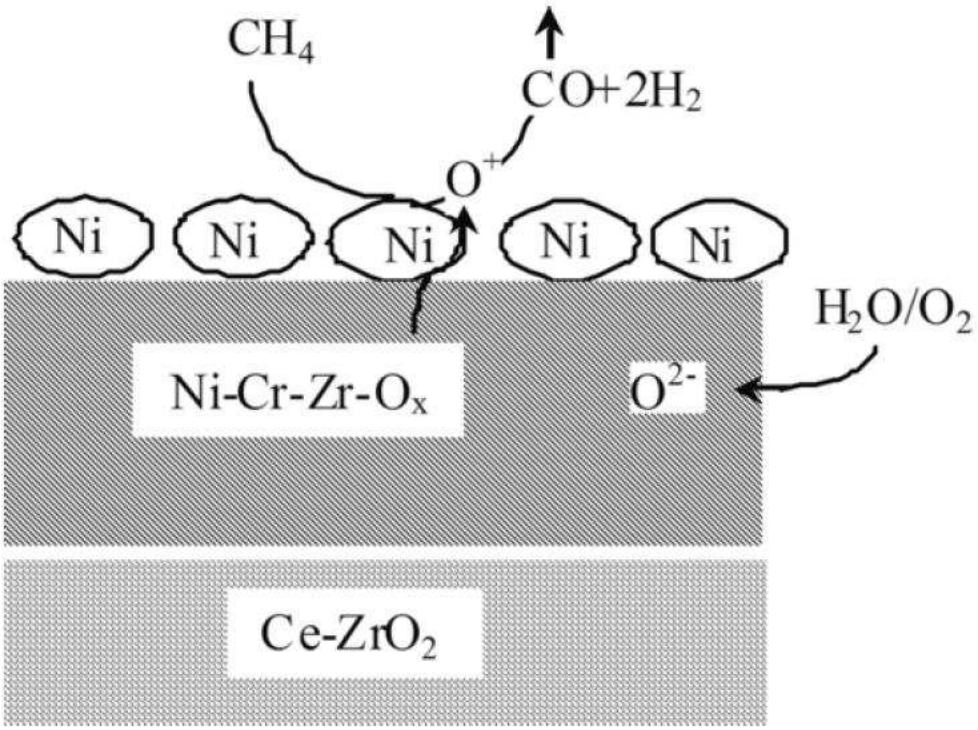

Fig. 6 Schematic of synthesis gas production over Ni/Ce–ZrO_2 catalyst [68].

Like Laosiripojana et al. [24], Lisboa et al. [73] reported high activity in ATRM over 10 wt% Ni supported on cubic phased Ce0.75Zr0.25O2 support obtained using the CP method by means of AM and AH as co-precipitating agents. The process performance was examined at 800 °C using S/C of 2.5 and O2/C of 0.5. The activity of the catalyst was attributed to a combination of metallic surface area and OSC of the support. Promotion effects of Ag, Fe, Pt and Pd in 10 wt% Ni supported on Ce0.5Zr0.5O2 prepared using the CP method, for utilization in ATRM was investigated by Dantas et al. [74]. The performance of the catalyst was studied over harsher conditions i.e 800°C with S/C of 0.5 and O2/C of 0.25. Addition of 1 wt% Ag was the best promoter. The catalyst reducibility along with the redox capacity of Ag containing catalyst was higher as compared to the bare Ni/Ce0.5Zr0.5O2 catalyst. Lower loading of 0.1 wt% exhibited lower activity in comparison to the 1 Ag wt% promoted catalyst. Two different methods of IMP were examined, with co-IMP exhibiting higher activity in comparison to sequential IMP.

Addition of Al2O3 to tetragonal Ce0.8Zr0.2O2 was shown by Roh et al. [50] to have a positive effect on performance of Ni supported catalyst in SMR. Escritori et al. [75] examined ATRM over Ni supported Ce0.5Zr0.5O2 prepared using the AHCP method, followed by co-IMP of γ-Al2O3 to provide 12 wt%/Ce0.5Zr0.5O2 modified Al2O3. Finally, a 10 wt% Ni was prepared by incipient wetness IMP of the modified support. The addition of Al2O3 favoured the formation of smaller Ni particles and better dispersion. The mix oxide based catalyst exhibited better reducibility compared to Ni/Al2O3. The presence of Ce–ZrO2 helped to avoid carbon deposits on the catalyst by providing an additional path for the adsorption and dissociation of oxygen and steam, forming O2− and OH− on the support surface. These groups removed the carbon deposits by reacting with them after they transferred to the metal-support interface. The presence of Zr in 10 wt%/Ni–

Zr10Ce20A170O2 was reported to prevent the formation of the catalytically inactive phase NiA12O4 and facilitate the dispersion of Ni, enhancing the activity of the catalyst [76].

2.2.2 Autothermal reforming of oxygenated compounds

De Lima et al. [77] reported high activity over 1.5 wt% Pt/Ce0.75Zr0.25O2 under ATR conditions in comparison to SR in hydrogen production from ethanol. ATR of ethanol ('ATRE') was performed using S/C of 1 and O2/C of 0.25 at 500 °C. In ATR conditions, decomposition of ethanol was inhibited or carbon monoxide oxidation was promoted. Further oxidative dehydrogenation of ethanol to form acetaldehyde was reported. In addition the oxidation of ethoxy species to acetate, followed by carbon dioxide formation as a result of decomposition via carbonates species, may use the oxygen from the support, as the vacancies were continuously replenished by oxygen from the feed. The presence of carbonate species on the catalyst surface were reported to be the reason for catalyst deactivation under SR conditions.

Youn et al. [69] examined the effect of Ce/Zr in ATRE using S/C of 1.5 and O2/C of 0.25 at 500 °C. The support was prepared using the templating SG method followed by impregnation to get a Ni supported catalyst. A 20 wt% Ni supported on Ce0.7Zr0.3O2 exhibited the best performance as a result of enhanced OSC of the support and the dispersion of Ni. The increase in Ce content beyond 0.7 resulted in lower activities due to excess oxygen provided by bulk ceria on the catalyst surface. Biswas and Kunzru [70] reported stable performance over 30 wt% Ni supported on Ce0.74 Zr0.26O2 catalyst in ATRE using S/C of 4 and O2/C of 0.5 in the temperature range of 400 to 650 °C. Addition of oxygen up to a certain value was reported to have a positive effect on the activity of the catalyst. No change in Ni particle size was found after the catalytic evaluation reporting insignificant sintering of Ni particles. Performance of CeO2–ZrO2 in ATR of biobutanol was examined by Cai et al. [78]. The authors evaluated the use of 6.5 and 0.4 wt% Co–Ir supported on 18 wt% ceria containing CeO2–ZrO2 oxide in ATR of simulated bio-butanol mixture using S/C of 3 and O2/mixture of 1.5 at 500 °C. The reducibility and OSC of the material affected the performance of the catalyst in descending order, following Co–Ir/18wt%CeO2–ZrO2>Co–Ir/ZnO>Co–Ir/TiO2.

Performance of Ce0.5Zr0.5O2–Al2O3 in ATRE was reported by Srisiriwat et al. [79] using S/C of 1.5 and O2/C of 0.13 at 700 °C. The addition of the mix oxide improved the dispersion of active Ni by inhibiting the interaction between Ni and Al2O3 support and promoting interaction between the support and the mix oxide. This addition of CeO2 and/or ZrO2 to Ni/Al2O3 enhanced the dissociation of intermediates from the oxygen fed into the system. This, further promoting the oxidation of hydrocarbons and carbon monoxide, produced from SRE to yield hydrogen and carbon dioxide. The oxygen intermediates effectively affected the (OSC) of the promoters, especially CeO2 ZrO2, by replenishing the oxygen vacancies in the ceria containing support, and in turn helping to reduce carbon formation. Kamonsuangkasem et al. [80] examined the use of 15 wt% Ni impregnated on 8%CeO2–ZrO2 modified Al2O3 in ATR of yellow glycerol. The best performance of the catalyst was reported over steam/glycerol and oxygen/glycerol molar ratios of 9 and 0.5 at 650 °C, respectively. The catalyst exhibited high oxidizing and reforming reaction activity.

In case of complex oxygenated hydrocarbons like ('PFAD'), Ni supported on the Ce0.75Zr0.25O2, SACP method using ammonia ('AM') as a co-precipitation agent, exhibited higher activity under ATR conditions in comparison to SR of PFAD. Shotipruk et al. [56] examined effect of O2/C in ATR of PFAD with fixed

S/C of 3 at 900 °C over 5 wt% Ni/Ce0.75Zr0.25O2. Increase in O2/C from 0 to 0.8 had a positive effect on hydrogen production, with higher ratios exhibiting no effect. The addition of oxygen was also shown to result in lower carbon formation formed from complex hydrocarbon fuels. Comparatively under same conditions Laosiripojana et al. [55] reported that with same metal loading, increase in O2/C increased hydrogen production in ATR of PFAD up to a O2/C value of 0.6 over Rh supported on Ce0.75Zr0.25O2 prepared by the same method. Higher O2/C had a negative effect on hydrogen production in comparison to no effect in case of a Ni based catalyst.

Table 6 below…

Table 6 Performance of Ce–ZrO_2 supported catalysts in terms of hydrogen production obtained in ATR of simple alkane and oxygenated hydrocarbons.

Author	Investigation	Catalyst	Conditions			Definition		Reported values			
			S/C	O_2/C	Temp (C)	Yield Y (%)	Selectivity S (%)	Y (%)	S (%)	Conversion (%)	Molar comp (%)
Laosiripojana et al. [55]	ATR of PFAD	5 wt% Rh -$Ce_{0.8}$ $Zr_{0.2}O_2$	3	0.6	900	18			100[a]	100[a]	–
Shotipruk et al. [56]	ATR of PFAD	5 wt% Ni–$Ce_{0.75}Zr_{0.25}O_2$	3	0.8	900	–		–	80[b]	100[b]	–
Srisiriwat et al. [79]	ATRE	15 wt%Ni–$Ce_{0.5}Zr_{0.5}O_2$–Al_2O_3	1.5	0.13	700		32		~63.5[c]	100[c]	–
Roh et al. [68]	ATRM	15 wt% Ni–$Ce_{0.2}Zr_{0.8}O_2$	1	0.5	750					99	–
Dong et al. [49]	ATRM	30 wt% Ni–$Ce_{0.74}Zr_{0.26}O_2$	1	0.5	750					95	
De lima et al. [77]	ATRE	1.5 wt% Pt/$Ce_{0.75}Zr_{02.5}O_2$	1	0.25	500	–	–		–	90[d]	55
Cai et al. [78]	ATR of biobutanol	6.5 wt% Co-0.4 wt% Ir/18 wt%-CeO_2–ZrO_2	3	1.5[a]	500	–	–	–	–	86	68.5
Ruiz et al. [72]	ATRM	1.5 wt% Pt–$Ce_{0.75}Zr_{0.25}O_2$	0.2	0.5	800	–	–	–	–	~70[e]	–
Youn et al. [69]	ATRE	20 wt%Ni -$Ce_{0.7}$ $Zr_{0.3}$ O_2	1.5	0.25	500		33		59	60[f]	
Cao et al. [71]	ATRM	30 wt% Ni–$Ce_{0.74}Zr_{0.26}O_2$	2	0.45	850	–	26	–	52.96	57.62[f]	–
Dantas et al. [74]	ATRM	1wt %Ag-10 wt% Ni -$Ce_{0.5}Zr_{0.5}$-Al_2O_3	0.5	0.25	800	–	–	–	80	55[g]	
Escritori et al. [75]	ATRM	10 wt% Ni -$Ce_{0.5}Zr_{0.5}$	0.5	0.25	800	–	–	–	–	>40[h]	~48[h]

table 6 continues..

		10 wt% Ni -$Ce_{0.5}Zr_{0.5}$-Al_2O_3								>65[h]	~46[h]
Laosiripojana et al. [24]	ATRM	10 wt% Ni -$Ce_{0.8}$ $Zr_{0.2}O_2$	3	1	800	–	–	–	30[h]	>50[i]	–
Lisboa et al. [73]	ATRM	10 wt% Ni -$Ce_{0.8}$ $Zr_{0.2}O_2$	2.5	0.5	800	–	–		50[b]	>50[b]	–

[a] The reported values were reported over 600 min.

[b] The activity was stable for about 50 h.

[c] The performance was evaluated for 400 min.

[d] The catalyst exhibited stable performance for 24 h.

[e] The reported conversion and selectivity were stable for 24 h.

[f] The value used is based on O_2/mixture molar ratio.

[g] The activity was stable for 11 h.

[h] Catalyst performance was evaluated for 6 h.

[i] The reported conversion and molar composition were stable for 24 h.

2.3 Catalytic partial oxidation

CPO over various noble and base metals supported on Ce–ZrO2 has been examined by Salazar-Villalpando et al. [81], Salazar-Villalpando and Miller [82] Salazar-Villalpando and Reyes [83], Larimi and Alavi [84], Silva et al. [85], and Silva et al. [86]. Investigations of ceria–zirconia supported catalyst in PO of hydrocarbon and oxygenated hydrocarbon are reviewed in the following sections.

2.3.1 Catalytic partial oxidation of methane (CPOM)

Salazar-Villalpando's group [81–83,87] examined the CPOM at 700 °C using O2/C of 5 over 1 wt% Rh, Pt and Ni supported on cubic Ce0.56Zr0.44O2, prepared by the CP method followed by hydrothermal crystallization. The Rh supported catalyst exhibited the highest activity as a result of the reducibility of material. Redox cycling of the material was shown to affect hydrogen generation by improving catalytic performance. Lattice oxygen was found to selectively oxidize methane to form carbon monoxide [87] through isotopic studies. Further, the presence of Rh accelerated the oxygen exchange with the support with maximum value observed at 250 °C. This was a result of oxygen spill over from the metal to the support. In comparison to the Rh supported catalyst, higher activity was found for Pt supported ones [82]. They reported that Ce anchored metallic Pt and helped in maintaining surface area along with prevention of migration and coalescence of Pt crystallites. PtO2 present in the catalyst was reduced by methane, decreasing the amount of PtO2 in the catalyst. Thus Pt reducibility was maintained thereby suppressing Pt sintering via formation of mobile and volatile PtO2. It was suggested that the high stability of Pt in Ce–containing supports under oxidizing conditions at high temperature was due to the formation of a Pt O Ce bond. This result was in contrast to that reported by de Lima et al. [63] in SRE using 1.5 wt% Pt/Ce0.75Zr0.25O2 catalyst.

Passos et al. [88] reported a different reason for higher stability of Pt supported catalysts in CPOM at 800 °C with O2/C of 0.5. They examined the performance of 1.5 wt% Pt over supports i.e. Ce0.75Zr0.25O2, Ce0.5Zr0.5O2 and Ce0.25Zr0.75O2 prepared by the CP method using ammonium hydroxide (AH) as a co-precipitating agent. Support reducibility and metal dispersion were the two important reasons for high stability of the Pt supported catalyst. The performance of the catalyst was also attributed to proper balance between OSC of the support and metal dispersion over the catalyst. The higher OSC of the material helped in removing the carbon deposits from the metal-support interface. Among the support formulations Ce0.5Zr0.5O2 exhibited lower deactivation in comparison to Ce0.75Zr0.25O2 and Ce0.25Zr0.75O2. A lower metal dispersion over the support decreased the metal-support interfacial area and hence the effectiveness of the carbon removal mechanism. Similar explanations regarding reducibility and OSC for high activity over 1.5 wt% Pt/Ce0.75Zr0.25O2 were reported by Mattos et al. [89,90] in CPOM at 800 °C using O2/C of 2. The supports were prepared by using the AHCP method. Combustion of methane was reported to be the first step during the process leading to the formation of carbon dioxide and steam, production of synthesis gas followed via DR and SR of the unreacted methane.

Similarly 3–5 wt% Pd/Ce0.7Zr0.3O2 exhibited high activity in CPOM between 700 and 900 °C, Fangli et al. [91]. The conversion over Pd catalyst was slightly lower compared to those over Pt and Rh ones. The activity of the catalyst was reported to be caused by higher dispersion of Pd and OSC capacity of the support. Unlike other noble metals i.e. Pt, Rh, and Pd, the supported Ru catalyst exhibited lower activity [92].

Performance of Pt supported on Ce0.75Zr0.25O2–Al2O3 catalyst was affected by Pt loading in CPOM at 800 °C with O2/C of 0.5, Silva et al. [85]. The doped support and active metal was prepared by the wet IMP method. The catalysts with higher dispersion (lower loading 0.5 wt%) promoted methane decomposition. Since the OSC of the support was not affected by Pt dispersion, the increased methane decomposition led to imbalance in the OSC and thus carbon deposition, leading to deactivation. In contrast, Silva et al. [93,94] found that 1.5 wt% Pt/Ce0.75Zr0.25O2–Al2O3 exhibited lower activity under the same conditions. The lower activity of the catalyst was attributed to lower surface coverage and OSC. Further, Zr incorporation in the ceria lattice was not achieved using the IMP method, affecting the activity of the catalyst. Similarly the activity of the catalyst was lower in comparison to Pt/CeO2/Al2O3.

The effect of support preparation methods on the performance of the catalyst was further examined by Silva et al. [86]. The supports were prepared with the PP and IMP methods, the latter providing higher surface coverage and resulting in higher stability and selectivity to hydrogen and carbon monoxide [86]. Under same conditions, addition of 1 wt% Ce to Al2O3, was shown by Silva et al. [95] to improve the performance of a Pt/Ce0.75Zr0.25O2–Al2O3 catalyst, by improving Pt dispersion, OSC, and coverage of Al2O3 by oxides. The addition of Ce helped in the formation of a more homogeneous solid solution affecting the performance as a result of higher OSC. The effect of Ce–Zr content on the performance of 1.5 wt% Pt/Ce0.5Zr0.5O2–Al2O3 in CPOM at 800 °C with O2/C was examined by Silva et al. [96]. Catalysts containing 10 to 20 wt% mix oxides were reported to form a solid solution, in comparison to 30 wt% which showed ceria rich and a zirconia rich phases, whereas 40 wt% exhibited a ceria rich phase and an isolated zirconia phase. Catalysts with 10 and 20 wt% Ce–ZrO2 had high activity in comparison to the others. The effect of support calcination temperature on the activity of 1.5 wt% Pt/Ce0.5Zr0.5O2–Al2O3 in CPOM was examined by Mortola et al. [97]. The supports were calcined at 800, 900, and 1000 °C with activity evaluation performed at 800 °C with O2/C of 0.5. Supports calcined at 800 and 900 °C showed slight decrease in activity in comparison to the significant decrease exhibited by the support calcined at 1000 °C. At all the calcination temperatures the supports showed formation of heterogeneous instead of homogenous solid solution. Surface area, degree of Al2O3 surface coverage by the ceria-based oxide, metallic dispersion, along with OSC decreased during the aging process at 800 and 900 °C. In addition to these effects, at 1000 °C ceria particle size increased as a result of sintering, deteriorating the stability of the catalyst. Although the supports aged at 800 and 900 °C affected the above properties of the catalyst, the reduction in these properties were not as significant as compared to those of the catalyst aged at 1000 °C, hence these catalyst exhibited higher activity and stability and selectivity to hydrogen and carbon monoxide.

Increase in Rh dispersion along with activity for WGS and oxygen mobility due to the presence of ceria, was reported as the cause of higher activity of Rh/Ce0.5Zr0.5O2 Al2O3. Boullosa-Eiras et al. [98] examined CPOM over 0.1 to 0.3 wt% Rh supported on Ce0.5Zr0.5O2–Al2O3 using O2/C 0.5 from 600 to 1250 °C. Further the high activity of the catalyst was also reported, due to the presence of stabilised Al2O3 along with the inhibition of α and CeAlO3 phases, which are known to be responsible for worse stability of CeO2 Al2O3 supported catalysts. Two different methods of preparation of the catalyst i.e. spray drying and slow evaporation were examined. Spray drying support had the highest thermostability in terms of sintering and phase transformation of the composites [99]. In addition to noble metals like Pt, and Rh, Ni supported on Ce0.7Zr0.3O2 Al2O3 was evaluated in CPOM by Qingwei et al. [100]. The performance of catalyst prepared by two different methods was examined in CPOM using O2/C of 0.5

between 600 and 900 °C. Catalyst formulation prepared by physical mixing of Al2O3 and Ce–ZrO2 displayed the poorest performance, while the catalyst prepared by AMCP of Ce(NO3)2 and Zr(NO3)2 (mix solution) along with Al(NO3)3, presented the best performance. But the carbon deposition on the catalyst prepared by the CP method was higher in comparison to the physically mixed formulation.

Like Rh/Ce0.56Zr0.44O2, the Ni supported catalyst was reported to require redox pre-treatments to reach higher catalytic activity [83]. The increase in activity in case of Ni was seen as a result of metallic re-dispersion and changes on the metal support interface. Dong et al. [101] and Roh et al. [102] reported divergent results over 15 wt% Ni supported Zr-rich supports (Ce0.2Zr0.8O2) prepared by the molten salt sol gel ('MSSG') method using O2/C of 0.5 between 600 and 800 °C. Dong et al. [101] performed CPOM using a pulse mechanism. Methane adsorbed on the Ni surface and dissociated to form hydrogen and carbon. The carbon then reacted with oxygen which was activated on Ni to form carbon monoxide. Similarly some carbon traveled to the interface of Ni Ce ZrO2 and Ni, reducing the support near the metallic Ni particle to produce carbon monoxide. Some of the carbon adsorbed on the metallic Ni was removed by the use of the lattice oxygen in the Ce ZrO2 support. The oxygen species was replenished by the gaseous oxygen. The dissociation of methane was enhanced as a result of the Ce0.2Zr0.8O2 support and improved carbon storage. Further, the mobility of oxygen promoted carbon removal from the catalyst surface. Larimi and Alavi [84] examined the performance of CPOM over 5 wt% Ni supported on Ce–ZrO2 prepared by the sodium hydroxide co-precipitation ('SHCP') method at 700 °C with O2/C of 0.5. Conversion of methane was reported to increase with Zr content, similarly to that reported by Dong et al. [49] and Roh et al. [102]. The increase in Zr content increased the catalyst surface area and Ni dispersion, thus increasing the activity of the catalyst. A catalyst formulation of Ce0.25Zr0.75O2 exhibited the best performance with least carbon deposition among the formulations examined. Under similar conditions, the results were very close to those reported by Wang and Xu [103] and Pengpanich et al. [104] over 10 and 15 wt% Ni supported on Ce0.25Zr0.75O2 obtained using AMCP and UH methods respectively.

Larrondo et al. [105] examined the performance of Ni supported on Ce0.9Zr0.1O2 in CPOM using O2/C 0.5 from 400 to 800 °C. They found the bare Ce0.9Zr0.1O2 support could be utilized as methane oxidation catalyst. Also, Ni/Ce0.9Zr0.1O2 acted as an oxidation catalyst up to 650 °C. Above 650 °C, the catalyst behaved as a CPO catalyst producing reformate with a H2/CO of 2. The mobility of oxygen in the material resulted in inhibition of carbon deposits. Higher Ni loading exhibited higher conversion. Villalpando et al. [83] reported that the Ni supported catalyst exhibited higher activity as a result of higher reducibility and surface area. The higher reducibility of the catalyst resulted in increased availability of surface lattice oxygen, which participated in the formation of carbon monoxide and hydrogen. Similarly the catalyst was reported to exhibit high ionic conductivity affecting the amount of carbon formed during the CPOM reaction at lower O2/C of 0.6. High oxygen mobility was also reported to accelerate surface carbon oxidation reactions, inhibiting carbon growth.

2.3.2 Catalytic partial oxidation of oxygenated hydrocarbons

In comparison to CPOM there are very few evaluations of hydrogen production over Ce–ZrO2 using ('CPOE') and other oxygenated hydrocarbons. CPOE at 300 °C and O2/C of 1 over 1.5 wt% Pt supported on Ce0.5Zr0.5O2 prepared using the AHCP method was examined by Mattos et al. [106]. The presence of ceria in the catalyst was responsible for the presence of methane and carbon dioxide via the

formation of acetate as a result of the OSC of the material. In contrast, the ZrO2 based catalyst was responsible for the formation of acetaldehyde via dehydrogenation of ethoxy species. The catalyst showed higher selectivity towards ethoxy species in comparison to the ceria based catalyst. A 1.5 wt% Pt/Ce0.75Zr0.25O2 prepared by the same method did not produce the desired hydrogen in CPOE at 500 °C with O2/C of 0.25 [77]. Instead, the catalyst had high selectivity towards acetaldehyde and carbon dioxide during CPOE. In a different investigation Wang et al. [107] reported that 20 wt% Ni supported on Ce0.8Zr0.2O2 prepared by glycine nitrate process demonstrated high activity in CPOE at O2/C of 1 in the temperatures range of 450 to 700 °C. Quite high selectivity to hydrogen was measured at 500 °C. The catalyst also displayed high resistance to carbon formation in SMR similar to the above applications. Ce0.75Zr0.25O2 was also found to have high activity in CPO of complex oxygenated hydrocarbons like palm fatty acids ('PFA'). Laosiripojana et al. [108] examined the performance of PO of palm fatty acid distillate (PFAD) at 850 °C with O2/C of 1 using a 5 wt% Ni supported on Ce0.75Zr0.25O2 prepared by the SACP method using urea as precipitating agent. The high activity of the catalyst prepared by the SACP method in comparison to the one prepared by the conventional CP method, was attributed to nano sized Ce–ZrO2 support and higher OSC and lattice oxygen mobility. The authors also reported that higher oxygen or temperature inhibited the formation of the higher hydrocarbons like ethylene, ethane, and propylene.

Table 7 below (2 pages)

Table 7 summarizes the performance evaluations of ~~various metal supported~~ Ce–ZrO_2 supported metal catalysts in CPO of simple alkanes and oxygenated hydrocarbons.

Table 7 Performance of Ce–ZrO_2 supported catalysts in terms of hydrogen production obtained in CPO of simple alkane and oxygenated hydrocarbons.

Author	Investigation	Conditions			Definition		Reported values			
		Catalyst	O_2/C	Temp (C)	Yield Y (%)	Selectivity S (%)	Y (%)	S (%)	Conversion (%)	Molar comp (%)
Laosiripojana et al. [108]	CPO of PFAD	5 wt Ni -$Ce_{0.8}Zr_{0.2}O_2$	1	900	20		70		100	–
Larrondo et al. [105]	CPOM	50 wt% Ni–$Ce_{0.9}Zr_{0.1}O_2$	0.5	650		28		~118	100	–
		9 wt% Ni–$Ce_{0.9}Zr_{0.1}O_2$						~108	90	
Pengpanich et al. [104]	CPOM	15 wt% Ni–$Ce_{0.25}Zr_{0.75}O_2$	0.5	750		29		91	98	–
Larimi and Alavi [84]	CPOM	5 wt% Ni–$Ce_{0.25}Zr_{0.75}O_2$	0.5	850				95	~98	–
Dong et al. [49]	CPOM	15 wt% Ni–$Ce_{0.2}Zr_{0.8}O_2$	0.5	800				99.6	98	
Fangli et al. [91]	CPOM	3.0 wt% Pt–$Ce_{0.7}Zr_{0.3}O_2$	0.5	800	–	–	–	–	92.8[a]	–
		5.0 wt% Pt–$Ce_{0.7}Zr_{0.3}O_2$							92.6[a]	
		1.0 wt% Pt–$Ce_{0.7}Zr_{0.3}O_2$							72.6[a]	
F. Silva et al. [95]	CPOM	1.5 wt% Pt/$Ce_{0.5}Zr_{0.5}O_2$/1 wt% Ce–Al_2O_3	0.5	800		–	–	60[a]	90[a]	–
F. Silva et al. [85]		0.5 wt% Pt/$Ce_{0.5}Zr_{0.5}O_2$/Al_2O_3						60[a]	90[a]	
		1.0 wt% Pt/$Ce_{0.5}Zr_{0.5}O_2$/Al_2O_3						60[a]	90[a]	
		1.5 wt% Pt/$Ce_{0.5}Zr_{0.5}O_2$/Al_2O_3						60[a]	90[a]	
Xu and Wang [103]	CPOM	10 wt% Ni–$Ce_{0.25}Zr_{0.75}O_2$	1.88	750	–	–	–	–	85	–
Salazar-Villalpando et al. [81]	CPOM	1 wt% Rh–$Ce_{0.56}Zr_{0.44}O_2$				–	–	90[b]	83[b]	
Roh et al. [102]	POM	1.5 wt% Pt–$Ce_{0.2}Zr_{0.8}O_2$	1.87	750				98	>80	–
F. Silva et al. [96]	CPOM	1.5 wt% Pt/10% $Ce_{0.5}Zr_{0.5}O_2$/Al_2O_3	0.5	800	–	–	–	95[c]	~70[c]	–

		1.5 wt% Pt/30% $Ce_{0.5}Zr_{0.5}O_2/Al_2O_3$						95[c]	~67[c]	
		1.5 wt% Pt/40% $Ce_{0.5}Zr_{0.5}O_2/Al_2O_3$						95[d]	~67[d]	
		1.5 wt% Pt/20% $Ce_{0.5}Zr_{0.5}O_2/Al_2O_3$						95[d]	~65[d]	
Mattos et al. [89,90]	CPOM	1.5 wt% Pt–$Ce_{0.56}Zr_{0.44}O_2$	0.5	800	–	–	–	~80[a]	>60[a]	–
Mortola et al. [97]	CPOM	1.5 wt% Pt/10%Ce–ZrO_2/Al_2O_3	0.5	1000	–	–	–	100[e]	60[e]	–
		1.5 wt% Pt/10%Ce–ZrO_2/Al_2O_3		900				~92[e]	~58[e]	
		1.5 wt% Pt/10%Ce–ZrO_2/Al_2O_3		800				~92[e]	~58[e]	
Passos et al. [88]	CPOM	1.5 wt% Pt–$Ce_{0.56}Zr_{0.44}O_2$	2	800	–	–	–	>80[b]	~60[b]	–
P Silva et al. [94]	CPOM	1.5 wt% Pt–$Ce_{0.5}Zr_{0.5}O_2$–Al_2O_3	0.5	800	–	–	–	~85	~52	–
		1.5 wt% Pt–$Ce_{0.25}Zr_{0.75}O_2$–Al_2O_3						~85	~52	
		1.5 wt% Pt–$Ce_{0.75}Zr_{0.25}O_2$–Al_2O_3						90	50	
		1.5 wt% Pt–$Ce_{0.75}Zr_{0.25}O_2$–Al_2O_3-imp[f]						90[f]	50[f]	
P Silva et al. [86]		1.5 wt% Pt–$Ce_{0.75}Zr_{0.25}O_2$–Al_2O_3-pp[g]						90[g]	50[g]	
Dong et al. [101]	CPOM	15 wt% Ni–$Ce_{0.2}Zr_{0.8}O_2$	0.5	800					27.4[h]	–
Salazar-Villalpando and Reyes. [83]	CPOM	1 wt% Ni–$Ce_{0.56}Zr_{0.44}O_2$	0.4–0.8	700	–	–		–	–	~4–5
		1 wt% Ni–$Ce_{0.56}Zr_{0.44}O_2$–redox pre						-	-	~9

[a] The activity was measured over period of 24 h.

[b] The activity was measured for 1200 min.

[c] The values were measured and were constant for the period examined.

[d] The values decreased within the evaluation of 24 h.

[e] The conversion and hydrogen selectivity for supports aged at 800 and 900 °C decreased slightly. While the samples aged at 1000 °C, decreased to 40 % by end of 24 h evaluation.

[f] Catalyst prepared by the IMP method. The catalytic activity in terms of conversion and selectivity was stable for 24 h.

[g] Catalyst prepared by the PP method. The conversion decreased to 20% within 24 h. While selectivity decreased to 40 % within 24 h.

[h] The results obtained are for one second pulse.

2.4 Dry reforming

Carbon dioxide has been identified as the most significant greenhouse gas arising from anthropogenic activities. Conversion of carbon dioxide is presently being explored as one potential alternative to its geological sequestration. Production of useful value-added products (chemicals products, fuels …) via syngas production and by dry reforming of methane ('DRM') has been investigated [109–113]. A major drawback of the process is formation of carbon over the catalyst surface. Ce–ZrO2 supported catalysts have been known to impart high activity in DRM as a result of high OSC of the support which generates active centers at the interface between metal and support, helping in decoking ability of the catalyst. In addition the presence of ceria has been shown to improve dispersion of the metal on the support, improving the catalytic activity.

Pt supported on ceria–zirconia catalyst exhibited poor performance in DRM at 600 °C with CH4/CO2 of 1. Damyanova et al. [114] examined the performance of 1 wt% Pt impregnated on CeO2 promoted ZrO2 with CeO2 content varying from 1 to 12 wt%, using CH4/CO2 ratio of 1 at 600 °C. Increase in ceria content from 1 to 12 wt% decreased CH4 conversion, while increase in ceria content from 1 to 6 wt% increased CO2 conversion and upon further increase in ceria content it decreased, finally yielding conversion values as low as 18% and 23% for CH4 and CO2 respectively. Similarly Chen et al. [115] found Rh supported on Ce0.752Zr0.25O2 catalyst exhibited a performance similar to Pt/CeO2–ZrO2 at 600 °C with CH4/CO2 of 1. The catalyst supports were prepared by SACP method. Increase in temperature and Ru loading resulted in higher catalytic activity. Higher Ru content (3 wt%) increased the activity of the catalyst due to higher Ru surface area. Lower loading (0.5 wt%) resulted in a strong interaction between support and metal, leading to lower availability of Ru for the reaction, and hence lower activity. However the increase in Ru loading above 1.5 wt% affected the stability of the catalyst by decreasing the surface areas and pore volumes of the catalysts. Formations of hydroxides were reported to occur during the reforming reaction responsible for carbon elimination. Unlike noble metals supported on Ce–ZrO2, Ni based catalysts have exhibited higher catalytic activity. Potdar et al. [116] assessed the use of 15 wt% Ni supported Ce0.8Zr0.2O2 catalyst in DRM prepared by a CP/digestion method. The authors compared the performance of a catalyst prepared using the CP method with an impregnated one at 800 °C using CH4/CO2 of 1. The catalyst prepared by the CP method exhibited the best performance. The high activity of the catalyst was due to higher surface
area of the nanosized support along with the better dispersion of NiO particles, and the strong integration of support and metal.

Roh et al. [117,118] examined the performance of DRM at 800 °C and CH4/CO2 of 0.96 over Ni catalyst prepared using the potassium hydroxide co-precipitation ('PHCP') method. The effect of support composition on the performance of the catalyst was investigated, with Ce0.2Zr0.8O2 and Ce0.5Zr0.5O2 showing severe deactivation as a result of carbon formation. Like Potdar et al. [116] they reported that Ni–Ce0.8Zr0.2O2 catalyst prepared by CP method, had the best performance among the compositions examined. The catalyst's performance was also better in comparison to the catalyst prepared by Ni impregnated on Ce0.8Zr0.2O2 support. Both groups examined the effect of loading on the catalyst performance, with 15 wt% Ni/Ce0.8Zr0.2O2 performing best among the catalysts prepared by both the methods. Higher loading resulted in carbon formation over the catalyst, attributed to lower Ni dispersion and higher Ni particle size. At similar conditions Jun et al. [119] also reported high activity over 15 wt% Ni/Ce0.8Zr0.2O2 formulation as a result of the combined effect of the nano crystalline cubic Ce0.8Zr0.2O2 support and the fine dispersion of the NiOx crystallites, leading to intimate contact between metal and support. Like Roh et al. [120], they examined the performance of Ce0.2–

Zr0.8O2/θ-Al2O3 in DRM at same conditions. Addition of Ce–ZrO2 to Al2O3 inhibited the transformation of Ni/θ-Al2O3 into NiAl2O4, and led to the formation of active NiOx thus imparting higher activity and stability to the catalyst. Under reforming conditions the catalyst was reported to be oxidized, which in turn reacted with deposited carbon, deoxidised by carbon dioxide dissociation. Increasing Ni loading from 3 to 6 wt% slightly affected the performance, but higher loading from 12 to 15 wt% had no effect.

Addition of Mg to Ce0.8Zr0.2O2 had a positive effect on the performance of the catalyst in DRM. Jang et al. [121] examined the performance using 15 and 10 wt% Ni and MgO over the supports at 800 °C. Addition of Mg to Ni/Ce 0.8Zr0.2O2 reduced the degree of reduction of the catalyst, and resulted in the formation of a solid solution between Ni and MgO. The basicity of MgO resulted in higher resistance of nickel to sintering and created intimate contact between Ni and MgO, causing a higher catalytic activity.

Co supported on Ce0.8Zr0.2O2 was also reported to exhibit high activity in DRM. Wang et al. [122] studied the use of 16 wt% Co supported on Ce0.8Zr0.2O2 prepared by the PHCP method, in DRM at 750 °C using CH4/CO2 of 1. The charge effect of CoOx species along with cubic Ce0.8Zr0.2O2 improved the reducibility of the sample. Further cubic Ce0.8Zr0.2O2 decreased the Co crystallite sizes and resulted in lower carbon deposition on the surface of the catalyst.

Kumar et al. [123] looked at the effect of catalyst preparation methods on the performance of 5 wt% Ni supported on ceria-zirconia catalyst in DRM at 700 °C with CH4/CO2 of 1. The catalyst supports were prepared using the SA aqueous AMCP method, and were compared with SG (alcogel) prepared supports followed by Ni IMP. The SA supports exhibited better performance than the alcogel prepared ones, due to higher surface area resulting in higher Ni dispersion on the support, along with better thermal stability. In comparison to the above authors [116,118,119], a 5 wt% Ni/Ce0.6Zr0.4O2 exhibited the best performance among the various compositions of supports prepared. Higher reducibility of the support enabled the support to make use of OSC and participate in redox reactions enhancing the stability of the catalyst. Unlike the above authors Ni on support prepared by the AMCP method exhibited lower activity.

The effect of surfactant addition to supports prepared using the AMCP method, in DRM was investigated by Sukonket et al. [124]. Catalyst supports prepared using higher surfactant/metal molar ratio exhibited higher activity. Performance of the catalyst was studied at 800 °C over 5 wt% Ni/Ce0.6 Zr0.4O2 using CH4/CO2 ratio of 1. Higher amount of surfactant led to a better dispersion of Ni on the catalyst leading to a stable catalyst formulation. The amount of surfactant affected the OSC of the catalyst, increasing with the amount of surfactant. The catalyst support prepared by metal/surfactant ratio of 1.25 possessed the largest numbers of both surface-active Ni sites and oxygen vacancies resulting in higher activity. Similar results were reported by Chen et al. [125] over 2 wt% Ni–Ce0.75Zr0.25O2 prepared using the 25% aqueous AMCP method, using CH4/CO2 of 1 in the temperature range of 700 to 900 °C. Methane conversion was shown to increase with rise in temperature. Addition of Ni to the solid solution in the co-precipitated catalyst resulted in better Ni dispersion and stronger interactions between Ni and the solid solution. Also the co-precipitated catalyst exhibited higher surface area and pore volume, resulting in the formation of catalyst with high activity along with higher resistance to coke formation and Ni sintering.

Matralis et al. [126] examined the DRM over 5 wt% Ni supports prepared by means of the AMCP method, with varying Ce/Zr ratio at 700 °C at CH4/CO2 of 1 without dilution. The authors reported that the Ce/Zr did not have a significant effect on the activity of the catalyst although surface areas and the surface of the metallic Ni varied considerably. Unlike Kumar et al. [123], Potdar et al. [116] and

Roh et al. [117], they reported that Zr rich supports had higher activity and higher resistance to carbon formation. Fig. 7 shows the mechanism of DRM over Ni based catalysts supported on mesoporous nanocrystalline ceria–zirconia solid solutions [127].

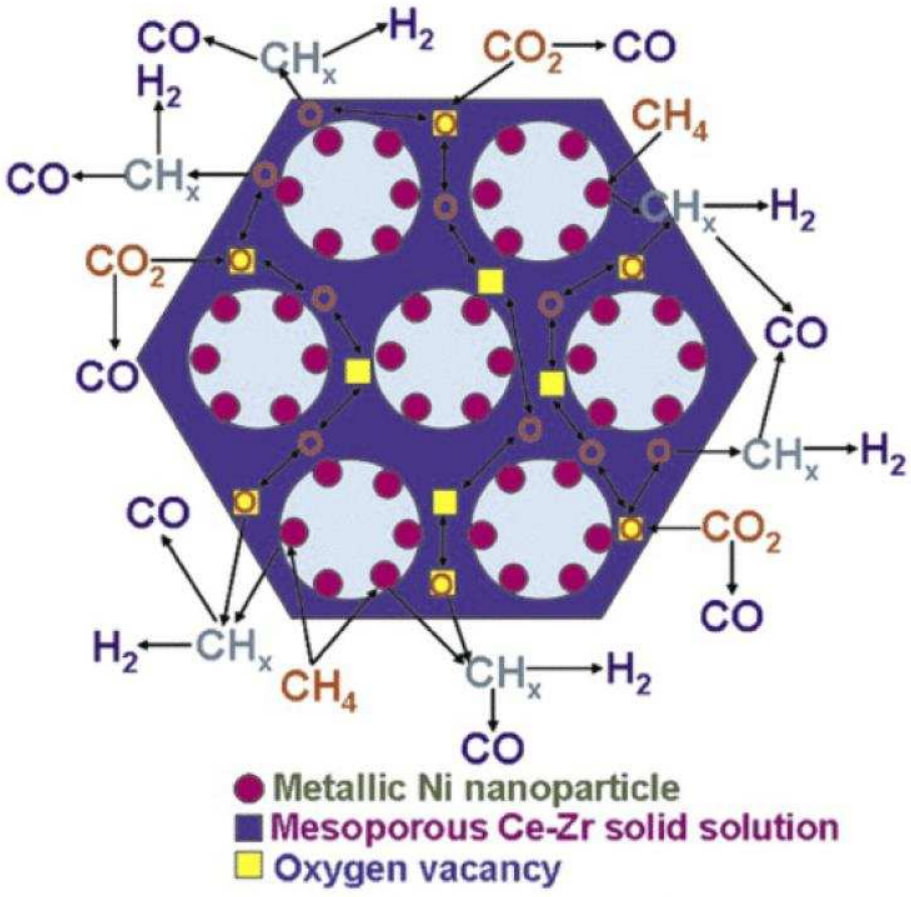

Fig. 7 Mechanism of the DRM over Ni based catalysts supported on mesoporous nanocrystalline ceria–zirconia solid solutions [127].

Most of the above authors utilized CP or SACP methods using various CP agents like PH and AM, but Črnivec et al. [128] compared the performance of Ce0.8Zr0.2O2 prepared using AMCP and glycothermal assisted methods for DRM. The performance of the catalysts were investigated at 800 °C using an undiluted mixture of methane and carbon dioxide. Materials synthesized using the CP method resulted in the formation of larger size crystallites of segregated CeO2 and ZrO2 oxides exhibiting poor activity and lower carbon resistance. In the glycothermal method, ethylene glycol and propanoic acid were reported to act as surface directing agents regulating the nanostructural assembly of the supports, resulting into a homogeneous nanocrystalline solid. The PP deposition method, used for laying down Ni on the support, resulted in the formation of smaller Ni particles; in comparison to the Ni particles obtained by the simple deposition method. The smaller Ni particles caused superior resistance to surface carbon and also displayed certain selectivity for the RWGS reaction. Table 8 summarizes the performance evaluations of Ce–ZrO2 supported metal catalysts in DR of simple alkanes and oxygenated hydrocarbons.

table 8 continued

Table 8 Performance of Ce–ZrO_2 supported catalysts in terms of hydrogen production obtained in DR of simple alkane and oxygenated hydrocarbons.

Author	Investigation	Conditions			Definition		Reported values			
		Catalyst	CO_2/CH_4	Temp (C)	Yield Y (%)	Selectivity S (%)	Y (%)	S (%)	Conversion (%)	Molar comp (%)
Jun et al. [119]	DRM	15 wt%Ni–$Ce_{0.8}Zr_{0.2}O_2$	0.98	800	–			95	98[a]	–
		15 wt%Ni–$Ce_{0.5}Zr_{0.5}O_2$			–			–	90[b]	
		15 wt%Ni–$Ce_{0.2}$ $Zr_{0.8}O_2$			–			–	91[c]	
		5 wt%Ni–$Ce_{0.2}$ $Zr_{0.8}O_2$			–			–	80[d]	

		10 wt%Ni–$Ce_{0.2}$ $Zr_{0.8}O_2$			–			–	85[d]	
		17 wt%Ni–$Ce_{0.2}$ $Zr_{0.8}O_2$			–			–	90[d]	
Roh et al. [117,118,120]	DRM	15 wt%Ni–$Ce_{0.8}Zr_{0.2}O_2$	0.98	800	–	–	–	–	98[d]	–
		15 wt%Ni–$Ce_{0.5}Zr_{0.5}O_2$							96[d]	
		15 wt%Ni–$Ce_{0.2}$ $Zr_{0.8}O_2$							95[d]	
Jang et al. [121]	DRM	15 wt%Ni–10 wt% MgO-$Ce_{0.8}Zr_{0.2}O_2$	1	800	–	–	–	–	96[e]	–
Potdar et al. [116]	DRM	30 wt%-CeO_2/10 wt%-ZrO_2	1	800	–	–		–	97[f]	
		15 wt%-CeO_2/10 wt%-ZrO_2							95[f]	
		10 wt%-CeO_2/10 wt%-ZrO_2							85[f]	
		5 wt%-CeO_2/10 wt%-ZrO_2							81[f]	
Sukonket et al. [124]	DRM	5 wt%Ni–$Ce_{0.6}Zr_{0.4}O_2$–1.25[g]	1	800	24	31		92.5[h]	85	–
		5 wt%Ni–$Ce_{0.6}Zr_{0.4}O_2$–0.8[g]						>92.5[h]	85	
		5 wt%Ni–$Ce_{0.6}Zr_{0.4}O_2$–0.5[g]						90[h]	85	
Chen et al. [115]	DRM	3 wt%Rh–$Ce_{0.75}Zr_{0.25}O_2$	1	800	–	–	–		~78	–
		1.5 wt%Rh–$Ce_{0.75}Zr_{0.25}O_2$							~72	
		1 wt%Rh–$Ce_{0.75}Zr_{0.25}O_2$							~68	
		0.5 wt%Rh–$Ce_{0.75}Zr_{0.25}O_2$							~53	
Wang et al. [122]	DRM	16 wt% Co–$Ce_{0.8}Zr_{0.2}O_2$	3	800	–	–	–	–	67	–
		16 wt% Co–$Ce_{0.5}Zr_{0.5}O_2$					–		56	
		16 wt% Co–$Ce_{0.2}Zr_{0.8}O_2$					–		46	
Kumar et al. [123]	DRM	5 wt%Ni–$Ce_{0.85}Zr_{0.15}O_2$–CTAB[i]	1	700	–	–	–	9[i]	65[i]	
		5 wt%Ni–$Ce_{0.6}Zr_{0.4}O_2$–CTAB						9[i]	64[i]	
		5 wt%Ni–$Ce_{0.92}Zr_{0.08}O_2$–CTAB[i]						92[i]	63[i]	
		5 wt%Ni–$Ce_{0.68}Zr_{0.32}O_2$–CTAB[i]						89[i]	62.[i]	
		5 wt%Ni–$Ce_{0.78}Zr_{0.22}O_2$–CTAB[i]						90[i]	62.2[i]	
		5 wt%Ni–$Ce_{0.4}Zr_{0.6}O_2$–CTAB[i]							60[i]	
Djinović et al. [110]	DRM	12 wt%NiCo–$Ce_{0.75}Zr_{0.25}O_2$–HT	1	800				–	62	–
		12 wt%NiCo–$Ce_{0.75}Zr_{0.25}O_2$–EG							58	
		6 wt%NiCo–$Ce_{0.75}Zr_{0.25}O_2$–HT							52	
		6 wt%NiCo–$Ce_{0.75}Zr_{0.25}O_2$–EG							50	
		3 wt%NiCo–$Ce_{0.75}Zr_{0.25}O_2$–EG							30	

3 Conclusion

Hydrogen production using Ce–ZrO2 supported catalysts during steam reforming, autothermal reforming, catalytic partial oxidation, and dry reforming of simple alkanes such as methane, and of oxygenated hydrocarbons like ethanol, glycerol, and acetic acid were reviewed. Among the processes examined steam reforming and autothermal reforming have demonstrated highest efficiencies and hydrogen yields. The performance of the Ce–ZrO2 catalyst is greatly affected by the method of preparation, surface area, metal dispersion and reducibility of the catalyst. Methods of catalyst preparation were shown to affect the oxygen storage capacity of the Ce–ZrO2 catalyst thus affecting its resistance to carbon deposition. Among the various evaluations, the co-precipitation method has been widely investigated in hydrogen production using all the process reviewed, in particular for the methane feedstock. Further addition of surfactant during the co-precipitation method helped to increase the surface area, and resistance to coke and to Ni sintering.

Only the steam and autothermal reforming processes have been investigated for hydrogen production from oxygenated hydrocarbons. Utilization of Ce–ZrO2 support for catalytic partial oxidation and dry reforming of oxygenated hydrocarbons has not been investigated extensively. A single hydrogen production evaluation via partial oxidation of PFAD over Ni/Ce–ZrO2 was reported. In the temperature range examined (450 to 900 °C), Ce rich (Ce≥0.5) catalysts were reported to be effective in steam reforming, autothermal reforming, and catalytic partial oxidation of oxygenated hydrocarbons. In the case of methane, different support compositions offered effective results at different temperatures. Noble metals and Ni supported on Ce rich (Ce≥0.5) supports were shown to be effective for steam methane reforming throughout the temperature range, while Ni supported on Zr rich (Ce≥0.2) were reported to be effective over 700 °C. Noble metal and Ni supported on Ce rich (Ce≥0.5) supports were effective in partial oxidation and autothermal reforming of methane and of oxygenated hydrocarbons. Conflicting results on Zr rich (Ce≤0.2) were also reported on both the processes. Only Ce rich (Ce≥0.5) supports were reported to be effective in dry reforming of methane. Addition of Zr to Ce to form Ce–ZrO2 solid solutions have shown to improve the performance of ceria as a support in hydrogen production. But redox capability, OSC, surface area, and thermal resistance of the material are not yet suitable for long term application and commercialization. Addition of Al2O3 to Ce–ZrO2 was shown to improve the properties of Ce–ZrO2 solid solution and help in cost reduction.

In case of alumina modified Ce–ZrO2 catalyst, the Zr rich (Ce≤0.2) catalyst was shown to be effective in steam reforming and dry reforming of methane. In autothermal reforming of methane and ethanol, alumina modified by Ce rich (Ce≥0.5) supports were shown to be effective, along with partial oxidation of methane.

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Appendix A

The definitions used by various authors are listed below.

A.1 Hydrogen yield definitions

Biswas and Kunzru [19] along with Roh et al. [60] defined hydrogen yield in SRE is as below.

$$Y_{H_2} = \left[\frac{(mol_{H_2})}{(mol_{C_2H_5OH})}\right] \quad \text{Eqn 17}$$

Dave and Pant [21] defined the yield of hydrogen in SRG as below.

$$Y_{H_2} = \left[\frac{(mol_{H_2})}{(mol_{C_3H_8O_3})}\right] \quad \text{Eqn 18}$$

Laosiripojana et al. [55] defined hydrogen yield in SR and PO of PFAD as below.

$$Y_{H_2}\,(\%) = \left[\frac{(\%H_2)}{(2(\%CH_4)+3(\%C_2H_6)+2(\%C_2H_4))}\right] \times 100$$

$$Y_{H_2}\,(\%) = \left[\frac{(X_{H_2})}{(2(X_{CH_4})+3(X_{C_2H_6})+3(X_{C_3H_6})+2(C_2H_4))}\right] \times 100 \quad \text{Eqns 19 -20}$$

Lin et al. [58] defined hydrogen yield in SRE by the following equation.

$$Y_{H_2}\,(\%) = \left[\frac{(mol_{H_2})}{(mol_{C_2H_5OH} \times 6)}\right] \times 100 \quad \text{Eqn 21}$$

Roh et al. [46] defined hydrogen yield in SMR by Eq. (22).

$$Y_{H_2}\,(\%) = \left[\frac{(F_{H_2out})}{(3 \times F_{CH_4in})}\right] \times 100 \quad \text{EQn 22}$$

Vagia and Lemonidou [65] defined hydrogen yield along with Yan et al. [54] and Zheng et al. [66] who defined hydrogen selectivity as below

$$Y_{H_2}\,(\%) = \left[\frac{(mol_{H_2})}{(mol_{CH_3COOH} \times 4)}\right] \times 100 \quad \text{Eqn 23}$$

Damyanova et al.[114] and Sukonket et al.[124] defined hydrogen yield in DRM as

$$Y_{H_2}\,(\%) = \left[\frac{(F_{H_2out})}{(F_{CH_4in})} \times \frac{1}{2}\right] \times 100 \quad \text{Eqn 24}$$

A.2 Hydrogen selectivity definitions

Dave and Pant [21] reported hydrogen selectivity as below

$$S_{H_2}\,(\%) = \left[\frac{(F_{H_2 out})}{(C \text{ atom in gas phase})} \times \frac{1}{RR}\right] \times 100$$

Eqn 25

Cao et al. [71] defined hydrogen selectivity by the following definition.

$$S_{H_2}\,(\%) = \left[\frac{(n_{H_2 \text{ produced}})}{((n_{H_2O \text{ converted}}) + (2n_{CH_4 \text{ converted}}))}\right] \times 100$$

$$H_2O \text{ (converted)} = (n_{CO \text{ produced}} + 2 \times n_{CO_2 \text{ produced}}) - (2 \times n_{O_2 \text{ consumed}})$$

Eqn 26-27

Larrondo et al. [105] defined hydrogen selectivity as below.

$$S_{H_2}\,(\%) = \left[\frac{(n_{H_2 out})}{\left(2(n_{CH_4 in} - n_{CH_4 out})\right.}\right] \times 100$$

Eqn 28

Pengpanich et al. [104] defined hydrogen selectivity as below.

$$S_{H_2}\,(\%) = \left[\frac{(n_{H_2 out})}{(n_{H_2 out} + n_{H_2O out})}\right] \times 100$$

Eqn 29

Roh et al. [60] defined hydrogen selectivity by Eq. (30).

$$S_{H_2}\,(\%) = \left[\frac{(n_{H_2 out})}{(n_{H_2 out} + 2n_{CH_4 out})}\right] \times 100$$

Eqn 30

Sukonket et al. [124] defined hydrogen selectivity by Eq. (31).

$$S_{H_2}\,(\%) = \left[\frac{(F_{H_2 out})}{(F_{H_2 out})_{\text{from DRM}} + (n_{H_2 out})_{\text{from complete SRM}}}\right] \times 100$$

Eqn 31

Srisiriwat et al. [79] defined hydrogen selectivity by Eq. (32).

$$S_{H_2}\,(\%) = \frac{F_{iout}}{\sum_i F_{iout}} \times 100$$

Eqn 32

Where Fi is flow rate of species i at outlet of the reactor.

Youn et al. [69] defined hydrogen selectivity by Eq. (33).

$$S_{H_2}\,(\%) = \left[\frac{(n_{H_2})}{((n_{C_2H_5OH in} - n_{C_2H_5OH out}) + (n_{H_2O in} - n_{H_2O out}))}\right] \times 100$$

Eqn 33

Conversion and molar composition in all most all the evaluations are defined as below

$$X\,(\%) = \frac{(\text{hydocaron})_{in} - (\text{hydrocarbon})_{out}}{(\text{hydrocarbon})_{in}} \times 100$$

Eqn 34

For e.g. in case of methane and ethanol conversion is defined as below

$$X(\%) = \frac{(\text{methane})_{in} - (\text{methane})_{out}}{(\text{methane})_{in}} \times 100$$ Eqn 35

$$X(\%) = \frac{(\text{ethanol})_{in} - (\text{ethanol})_{out}}{(\text{ethanol})_{in}} \times 100$$ Eqn 36

Dave and Pant [21] defined conversion differently than the common conversion definition.

$$\text{Glycerol conversion}(\%) = \left[\frac{(C \text{ atoms in gas phase})}{\text{carbon in feed}}\right] \times 100$$ Eqn 37

$$M_p(\%) = \frac{\text{mol}_p}{\sum \text{mol}_{sp}} \times 100$$ Eqn 38

where the moles of each product are given mol_p and mol_{sp} is the total moles of products.

While Abreu et al. [51] defined hydrogen molar composition as

$$M_p = \frac{\text{mol}_{H_2 \text{ produced}}}{\text{mol}_{CH_4 \text{converted}}}$$ Eqn 39

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