



# 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') is 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 production from SR and ATR of ethanol and glycerol and in steam methane reforming (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 temperatures i.e. above 700 °C. 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.

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**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; O<sub>2</sub>/C, molar oxygen to carbon ratio; 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; PP, precipitation; RME, reverse micro-emulsion; S, support; SA, surfactant assisted; SACP, surfactant assisted co-precipitation; S/C, molar steam to carbon ratio; SG, sol gel; SIMP, sequentially impregnated; SCCP, sodium carbonate co-precipitation; 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

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## 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 many 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  $Ce^{3+}$  and  $Ce^{4+}$  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 lattice 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 found to convert poisonous methanethiol ( $CH_3SH$ ) to hydrogen-rich gas via the solid-gas reaction between ceria and methanethiol [18]. In the presence of steam, formation of  $Ce(SO_4)_2$  was described 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 a cube, each anion being tetrahedrally coordinated by four cations. This makes ceria's structure more stable and prevents the conversion of  $Ce^{4+}$  to  $Ce^{3+}$  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 the endothermic SR process is carried out at high temperature i.e. 800 °C or higher, resulting in the decrease of 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  $Ce_{0.75}Zr_{0.25}O_2$  obtained by zirconium doped ceria is shown in Fig. 1. Fig. 1(a) shows the side view and (a\*) represents the top view of the  $Ce_{0.75}Zr_{0.25}O_2$  oxide [28]. Fig. 2 shows a high resolution transmission electron microscopy (HRTEM) image of  $Ce_{0.75}Zr_{0.25}O_2$  prepared using the decomposition and co-precipitation method [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%  $CeO_2$ - $ZrO_2$  are shown in Fig. 3 [36].

Tables 1 and 2 show the effects of the preparation method on the surface area, OSC, and metallic dispersion of Ce-ZrO<sub>2</sub> 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-ZrO<sub>2</sub> catalysts prepared by varied methods, utilized in hydrogen production processes.

The inclusion of  $Zr^{4+}$  or  $Hf^{4+}$  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  $Ce^{4+}$  to the support surface takes place, resulting in the formation of a 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  $Ce^{4+}$  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  $Ce^{4+}$  is known to increase with Zr/Ce ratio. The effect of

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